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Mechanistic insight in the propylene derived distinct NO uptake and release behaviors on Pd/SSZ-13 for low-temperature NO adsorption

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ABSTRACT

Pd/SSZ-13 catalysts were investigated for the simultaneous storage of NO and C_3H_6 at 100 °C. The effects of the state of Pd species on co-adsorption and release were studied under simulated exhaust conditions. The catalysts were characterized by NH₃-TPD, XRD, and TEM for Pd²⁺ and PdO species. NO adsorption/release behavior is impacted by the nature of reactants and the NO storage capacity at 100 °C was enhanced by simultaneous NO + C_3H_6 adsorption. DRIFTs results showed that Pd²⁺ provides the adsorption sites for NO + C_3H_6 to form Pd²⁺(NO) (C_3H_6), which alleviates the inhibition effect of H₂O on NO adsorption and effect of intermediate CO, depend on whether NO was adsorbed alone or together with C_3H_6 . The mechanistic pathways during different stages of NO + C_3H_6 co-adoption and release are proposed.

1. Introduction

Diesel oxidation catalysts (DOC) and selective catalytic reduction (SCR) of NO_x or lean NO_x traps (LNT) are major units for effectively eliminating gaseous hydrocarbons (HCs), CO, and NO_x , once the temperature in the exhaust reaches the light-off of these catalysts [1–6]. However, in practical applications, a high portion of the vehicle emissions is emitted during the cold start period of the engine when the catalysts are not yet warmed up [7,8]. To meet the increasingly stringent regulations, it is necessary to directly eliminate NO_x from the exhaust at the low temperatures encountered during cold start. The temporary storage of NO_x is a promising approach to control the cold start emissions below 150 °C [7,9–12]. The stored NO_x is released once the exhaust temperature has increased and is subsequently converted by the downstream catalysts.

Since the pioneering study by Chen *et al.*, Pd/SSZ-13 catalysts have attracted widespread interest as low-temperature NO adsorbers [13–15]. Pd^{2+} cations are believed to act as NO trapping sites by forming $Pd^{n+}(NO)$ (n = 1 and 2) intermediates [13,16–20]. As a result, it is important to maximize Pd^{2+} cations to improve the NO storage

capability of Pd/SSZ-13 [13,17,21]. Ryou et al. [22,23] found that the hydrothermal treatment of Pd/SSZ-13 (Si/Al = 23) at 750 $^{\circ}$ C, which was prepared by the incipient wetness impregnation method, could significantly improve the performance of NO storage at low temperatures because the hydrothermal treatment generates more Pd²⁺ cations likely via the protonolysis of PdO species that are inactive for NO adsorption [9,13,16]. The use of a low Si/Al ratio is another option for increasing the relative Pd^{2+} loading in the zeolites. Khivantsev *et al.* [17] reported that 100 % Pd^{2+} dispersion was achieved by using a modified impregnation method for loading 1 wt% Pd on SSZ-13 (Si/Al = 6). However, when the Pd loading increased to 3 wt%, PdO particles could clearly be observed [17]. In this case, the Pd/Al ratio in the Pd/SSZ-13 catalyst was approximately 0.15, much lower than the ideal Pd/Al ratio of 0.5. Previous results also found that the formation of metal oxides such as CuO seems inevitable for Cu/SSZ-13 SCR catalysts that are prepared by the solid-state ion-exchange method [24], because the metal salts tend to agglomerate to form metal oxides at elevated temperatures even though numerous sites are still available for cation exchange. Nevertheless, the loading of metal cations in zeolites by solid state ion-exchange is still a cost-effective preparation method [25] particularly for the full

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utilization of precious Pd metals.

Water vapor, which is always present in vehicle exhaust, impedes the NO adsorption over Pd/SSZ-13 [16,26]. DRIFTs showed that NO molecules originally adsorbed on Brønsted acid sites (forming NO⁺ at 2151 cm⁻¹) are displaced by the water molecules, whereas the intensity of IR peaks for NO adsorbed on the Pd cations can be largely maintained [13,27] compared with the spectra in the absence of water vapor. However, a study by Khivantsev *et al.* [16] showed that the NO/Pd ratio on Pd/SSZ-13 with 100 % Pd²⁺ ion dispersion cannot reach 1.0 when NO is co-fed with water. The competition of H₂O with NO adsorption is likely due to bonding with Pd²⁺ ions to form Pd(H₂O)₂(O-Z)₂ or [Pd (OH)₄]²⁻/[Pd(OH)₃(H₂O)]⁻).

CO also has an impact on NO adsorption. Negative effects on the NO adsorption capacity of Pd/SSZ-13 and Pd/Beta were observed by Ryou et al., Yao et al., and Gu et al. [28-30], respectively, when CO was present in the feed as a reductant. It was found that, even with O₂ in feed, the presence of CO still induced significant deactivation of Pd/SSZ-13 and Pd/Beta [29,30]. The presence of CO was found to agglomerate Pd^{2+} ions into large Pd particles that existed on the external surface of SSZ-13, which cannot be reversed by oxidative treatments [28]. Although the integration of a model DOC can alleviate the CO-induced deactivation of PNAs [31], the CO poisoning effect should be seriously addressed, as this is what is stopping PNA materials from being commercial. It was also reported that, when the feed gases included both CO and water, the NO adsorption capacity on Pd/zeolites below 100 °C increased [16,21,32–34]. Actually both CO and NO can be simultaneously adsorbed on Pd/SSZ-13 at low temperature (100 °C) [16,17,21]. The FTIR results of Khivantsev et al. attributed NO and CO co-adsorption to their association with Pd^{2+} ions and the subsequent formation of a Pd²⁺(NO)(CO) complex, which was proposed to suppress the reaction of Pd^{2+} with water forming $Pd(H_2O)_2(O\text{-}Z)_2$ (NO: Pd ratio is around 1) [16,17]. It has also been proposed that the improvement of NO adsorption at set uptake temperature (approximately 100 °C) by CO was attributed to the reduction of hydrated Pd²⁺ to Pd⁺, as indicated by the detection of CO₂ was detected during NO + CO co-adsorption on Pd/ SSZ-13 at 100 °C [26,33,35].

Hydrocarbons, which are always present in vehicle exhaust, also impact the NO adsorption over Pd/SSZ-13 [33,36-40]. In recent decades, it has been found that zeolites have the ability to store HCs at temperatures below 200 °C, while the presence of H₂O was found to be detrimental for HC storage [7,41]. The adsorption capacity for propene and toluene, representative of small alkenes and aromatics, increased with decreasing Si/Al ratio of the zeolites [42], providing evidence for specific interactions between HCs and acid sites. Yoda et al. [43] found that a hydrogen bond formed between the π -electrons of the alkene (C=C) and H^+ of the -Si-O(H^+)-Al is responsible for the chemisorption of HCs on the zeolites. Furthermore, Lewis acid sites can be beneficial for trapping HCs [7]. Doping zeolite with metal ions can provide additional Lewis acid sites, thereby improving the HC adsorption capacity. For example, Ag^+ , Pt^{2+} , and Cu^{2+} doping resulted in enhanced adsorption capacity due to the formation of Ag⁺-phenyl, Pt²⁺-C₂H₄ and Cu²⁺-C₂H₂ complexes in the channels of zeolites [44–46]. In addition, Pd^{2+} exchanged zeolites show C2H4 adsorption capacity on Pd/Beta and Pd/ SSZ-13, while the H-SSZ-13 exhibited no C2H4 adsorption [11,33,47,48], indicating the adsorption of C₂H₄ on ionic Pd. FTIR results [49] further showed the transformation of $Pd^{2+}(NO)$ to $Pd^{2+}(NO)$ (C₂H₄) complex after Pd/SSZ-13 that had adsorbed NO was exposed to C₂H₄, indicating NO and HCs co-adsorption The strong interaction between C_2H_4 and Pd^{2+} ions increased the NO storage content at a fixed uptake temperature (around 100 °C), which also shifted the NO_x release to higher temperatures in Pd/SSZ-13 [33,36]. It was also reported that Pd/SSZ-13 exhibited different NO uptake/release features in the presence of NO + C_2H_4 , $C_{10}H_{12}$, toluene, and $C_{12}H_{26}$ respectively [33,36,39]. This clearly demonstrates that the types of HCs impact the chemistry occurring in co-adsorption/release of NO + HCs on Pd/SSZ-13.

 C_3H_6 is a representative low chain HC in the exhaust important. NO $+\ C_3H_6$ uptake/release on Pd/Beta was investigated in previous works [11,38,47,50]. Recently, Kunal *et al.* [51] evaluated the effect of C_3H_6 on NO adsorption and release characteristics on Pd/SSZ-13, in a simple feed that containing NO and C_3H_6 during adsorption while only including basis gases (CO₂ + H₂O + O₂) in release period; they found that the presence of C_3H_6 improved the NO uptake at 100 °C (NO: Pd ratio increased from 0.27 to 0.51) and increased the NO release temperature. However, some important information, such as C_3H_6 adsorption and release characteristics, are not provided. More importantly, the mechanism for the effect of C_3H_6 on PNA behaviors of Pd/SSZ-13 is still not clear.

In this work, we investigated the effect of C_3H_6 on NO uptake and the thermally-induced release of the stored molecules on Pd/SSZ-13 at low temperature under simulated exhaust gas conditions (with the NO and C_3H_6 always present). Herein, we show that the NO_x adsorption/release characteristics in co-adsorption of NO and C_3H_6 were quite different from those when NO was adsorbed without C_3H_6 . The NO storage capacity was enhanced by C_3H_6 at 100 °C, and the stored C_3H_6 was converted efficiently during the release period (at elevated temperatures) without desorption. The effects of CO intermediate and oxidation reactions have been investigated, and the results were discussed in light of the chemistry of the adsorption of NO, C_3H_6 , and the intermediate CO.

2. Experimental

2.1. Catalyst preparation

Na-SSZ-13 (Si/Al = 6, determined by ICP-MS) was synthesized by a 5 L autoclave according to the previously reported procedures [52]. The Pd/SSZ-13 catalysts were prepared by incipient wetness impregnation. First, the calcined Na-SSZ-13 was transformed to NH₄-SSZ-13 via ionexchange with a 5 M (NH₄)₂SO₄ solution at 80 °C for 2.5 h. NH₄-SSZ-13 was then impregnated by an appropriate amount of palladium nitrate solution (Alfa Aesar) to make Pd/SSZ-13 with 2 wt% Pd loading. The wetted catalyst precursor was dried under ambient conditions for 6 h and then dried at 60 °C for 8 h. Finally, the catalysts were obtained by the calcination of precursors by heating in air to 275 $^\circ$ C at a rate of 1 $^\circ$ C/ min holding at 275 $^\circ \rm C$ for 30 min, followed by further heating to 650 $^\circ \rm C$ at a ramp of 2 °C/min, and holding at 650 °C for 5 h. These Pd/SSZ-13 catalysts were denoted as 2 Pd. The ICP results showed that the total Pd content in the 2 Pd catalysts was 1.97 wt%, corresponding to a Pd/Al ratio of 0.1. A H-SSZ-13 sample was also prepared by calcining NH₄-SSZ-13 at 650 $^\circ \rm C$ in air for 5 h.

2.2. NO (C_3H_6) storage and release

The storage and release experiments of NO or C₃H₆ or simultaneous $NO + C_3H_6$ were carried out in a fixed-bed quartz tube reactor (4 mm inner diameter) under a simulated realistic (5 % H₂O-5 % CO₂) exhaust condition. The gas flow rates were adjusted by mass flow controllers. The catalyst temperature was controlled and measured by two K-type thermocouples located upstream and downstream of the catalyst bed. Deionized water was fed by a p-Series syringe pump (Teledyne Isco). To fully vaporize liquid water, the main gas tubing was wrapped by heating tapes to keep the entire lines down to the FTIR gas analyser isothermal at 120 °C. Typically, in each test, 50 mg of powder catalyst (250–420 μm) was used and was diluted with the same size silica gel (50 mg, Sigma Aldrich Davisil Grade, calcined at 800 °C for 4 h). Prior to the storage experiments, the gas mixture was adjusted and maintained during the entire course of storage and release to contain 200 ppm NO, 200 ppm C_3H_6 (when applied), 5 % H_2O , and 5 % CO_2 (balanced with N_2). The gas concentrations (NO, CO, C_3H_6 , CO₂, NO₂, N₂O, and H₂O, etc.) during the entire storage and release stages were measured online by a gas FTIR analyzer (Antaris[™] IGS).

The pretreatment of the Pd/SSZ-13 catalyst and the procedures for

storage and release are schematically shown in Fig. S1. Typically, in each test, the catalyst was first pretreated at 600 °C with a flow of 10 % O_2/N_2 for 30 min and another 30 min with a flow of 10 % O_2-5 % H_2O-N_2 at a rate of 250 mL/min. Then, the catalyst was cooled to 100 °C for storage under the same feed rate that corresponded to a weight hourly space velocity (MHSV) of 300,000 mL·h⁻¹·g⁻¹. Before the NO adsorption at 100 °C, the concentrations in the gas mixture were first stabilized and measured in a bypass line of the reactor. Upon flow stabilization, the gas flow was switched from bypass to the catalyst bed and maintained for gas adsorption for 10 min (NO only) or for 15 min (NO + C₃H₆ coadsorption) to ensure that the adsorption equilibrium had been reached. This adsorption stage was then followed by a release stage where the temperature increased to 600 °C at a ramping rate of 10 °C/ min under the same gas mixture feed.

2.3. Catalytic oxidation of C₃H₆ and CO

To investigate the catalytic oxidation activity of the Pd/SSZ-13 catalyst, light-off experiments of CO and C_3H_6 oxidation were carried out in the same reactor system. Typically, 25 mg of the catalyst was diluted with 25 mg of silica gel and a gas mixture containing 200 ppm CO or C_3H_6 , 10 % O_2 , 5 % H_2O , and 5 % CO_2 was fed. The total flow rate was kept at 250 mL/min, which corresponded to a WHSV of 600, 000 mL·h⁻¹·g⁻¹. Prior to the test, the catalyst was first pretreated at 600 °C in a 10 % O_2/N_2 flow for 30 min, and then the gas was switched to a flow containing 10 % O_2 and 5 % H_2O in N_2 at 600 °C for another 30 min prior to cooling down to 100 °C. The Pd/SSZ-13 was stabilized in the reaction feed gases containing 200 ppm CO or C_3H_6 at 100 °C before light-off. The light-off runs started from 100 °C with a ramping rate of 2 °C/min. The concentrations of reactants and products were analyzed online by FTIR spectroscopy (AntarisTM IGS). The conversions of CO and C_3H_6 are calculated by the following equations.

C3H6 conversion =
$$\left(1 - \frac{[C_3H_6]_{out}}{[C_3H_6]_{in}}\right) \times 100\%$$
 (1)

$$CO \ conversion \ = \left(1 - \frac{[CO]_{out}}{[CO]_{in}}\right) \times 100\%$$
(2)

2.4. Comparison of C_3H_6 oxidation with and without NO

To investigate the influence of NO on the catalytic activity of Pd/SSZ-13, the C_3H_6 oxidation reaction was compared with and without NO using the same reactor system under steady state conditions at 230, 260, 300, 330, and 400 °C. In these cases, 50 mg of catalyst was diluted with 50 mg of silica gel. All pretreatment procedures were the same as those in the light-off tests prior to cooling 100 °C. The catalyst bed was kept at each temperature for reaction while the inlet gas composition was varied according to the following sequence (also shown in Fig. 6):

Step 1: 200 ppm C_3H_6 -10 % O_2 -5 % H_2O -5 % CO_2 - N_2 for 20–30 min; Step 2: 200 ppm C_3H_6 -200 ppm NO-10 % O_2 -5 % H_2O -5 % CO_2 - N_2 for 20–30 min;

Step 3: 200 ppm C₃H₆-10 % O₂-5 % H₂O-5 % CO₂-N₂ for 20-30 min.

2.5. Catalyst characterization

 N_2 physisorption was carried out at -196 °C on a Micromeritics ASAP 2020 instrument to determine the specific surface area and pore volume of the catalysts. Prior to the analysis, the sample was predegassed in vacuum at 350 °C for 24 h. The specific surface area was calculated using the BET equation; the micropore surface area and micropore volume were estimated using the *t*-plot method. Powder Xray diffraction (XRD) measurements were carried out on a Rigaku Ultima IV instrument using Cu K α radiation ($\lambda = 1.54178$ Å) at 40 kV and 44 mA under ambient conditions. The scan angle was set from 5° to 55° using a step size of 0.01°, and data were accumulated at a rate of 0.083°/



Fig. 1. NH₃-TPD profiles of the Pd/SSZ-13 and H-SSZ-13 samples.

s. Pd particles were imaged by a JEOL 2010F transmission electron microscope (TEM) with an accelerating voltage of 200 kV. Before taking the images, the powder catalyst was suspended in ethanol, dispersed by ultrasonication, and then dropped onto lacey formvar/carbon 200 mesh copper grids (Ted Pella, Inc).

To assess the surface acidity and Pd status due to Pd loading in SSZ-13, NH₃ temperature-programmed desorption (NH₃-TPD) was performed using a fixed bed reactor (10 mm in diameter) equipped with an FTIR analyzer (Nicolet iS10) for product analysis. Typically, 100 mg of catalyst was used and preheated at 600 °C for 1 h in a 10 % O₂/N₂ flow (500 mL/min). Then the catalyst was cooled to 200 °C under the same flow rate prior to cooling to 100 °C in a flow of N₂. At 100 °C, the gas was switched from N₂ to a flow of 500 ppm NH₃/N₂ (500 mL/min) for 1 h. Then the catalyst was purged by a N₂ flow to remove weakly adsorbed NH₃ at 100 °C till NH₃ was no longer detected. Subsequently, NH₃-TPD was conducted by heating the catalyst in N₂ from 100 °C to 600 °C with a ramp of 10 °C/min.

In situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTs) was used to identify adsorbed species and intermediates. DRIFTs experiments were conducted on a Bruker Tensor 27 spectrometer equipped with an MCT detector cooled by liquid nitrogen. The Pd/SSZ-13 catalyst, which was ground by mortar grinding, was loaded into a reactor cell (Praying MantisTM) that has two ZnSe windows and a quartz window. Prior to collection of background spectra at the desired temperatures, the catalyst was pretreated at 550 °C for 1 h in flowing 20 % O_2/N_2 .

3. Results

3.1. State of Pd species in Pd/SSZ-13

Generally, for zeolite catalysts prepared by solid-state ion exchange, there are different species that always co-exist after calcination. These species mainly include cations in the exchange sites and metal or metal oxides in the channels of zeolites. The exchanged Pd species (*i.e.*, Pd cations) occupy the Brønsted acid sites while the non-exchanged Pd species exist in the form of PdO particles (after calcination at 650 °C in air) on the exterior surface or in the cages of SSZ-13. Although it was reported that PdO particles are inactive for adsorbing NO and that the NO storage efficiency decreases with increasing Pd loading because the ratio of Pd²⁺ to total Pd in SSZ-13 is less than 1.0 [13], PdO particles are very active sites for HCs oxidation over Pd/SSZ-13 catalysts that were prepared by incipient wetness impregnation [53]. Therefore, the

Table 1

Surface areas and pore volumes of the samples.

Sample	Surface area (m ² /g) BET Micropores	Pore volume (cm ³ /g) Total Micropore
H-SSZ-13	529 515	0.283 0.257
2 Pd	430 419	0.242 0.226



Fig. 2. XRD patterns of different samples after calcination at 650 $^\circ \rm C$ in air for 5 h.

presence of PdO species in the Pd/SSZ-13 catalyst may have an impact on the performance of simultaneous NO and C_3H_6 storage and release under the reaction conditions.

3.1.1. Pd cation species in Pd/SSZ-13

To identify Pd cations on the acid sites of Pd/SSZ-13 catalysts, NH₃-TPD was carried out and the results are shown in Fig. 1. Two NH₃ desorption peaks were observed on H-SSZ-13: one peak centered at 160 °C (peak A) and another peak at 450 °C (peak C). The peak at 160 °C corresponds to the NH₃ desorption from weak acid sites the weak Lewis, such as extra-framework Al sites [54]; the peak at 450 °C is attributed to NH₃ desorption from Brønsted acid sites [6]. After Pd loading, the NH₃ desorption characteristics on the weak Lewis sites were similar to those on H-SSZ-13 whereas the original peak of NH₃ desorption on the Brønsted acid sites (peak C at around 480 °C) was decreased, indicating that the Brønsted acid sites in H-SSZ-13 are occupied by Pd cations. Meanwhile, a third NH₃ desorption peak at 325 °C (peak B) was generated on the 2 Pd sample. This peak should reflect NH₃ adsorption on the Pd cations, as the NH₃ on Pd ions (Pd²⁺(NH₃)_x) are typically decomposed in 200–500 °C [55].

3.1.2. Pores, crystallographic structure, and TEM images

After calcination at 650 °C for NH4-SSZ-13 transformation to H-SSZ-13, a high BET surface area of 529 m²/g was maintained, 97 % of which was contributed by micropores, as shown in Table 1. After Pd loading, the BET surface area decreased by 19 % and the total pore volume decreased by 14 % accordingly for the 2 Pd catalyst. Particularly, the micropore volume in the 2 Pd catalyst decreased by 12 %, indicating that the pore volume loss after Pd loading should be primarily attributed to the blockage of small cages in SSZ-13 by Pd species. These results demonstrate that in addition to Pd²⁺, some of the Pd species might exist in the form of PdO particles that stay in the cages of SSZ-13.



Fig. 3. Scanning TEM images of the 2 Pd.



Fig. 4. (a) NO adsorption at 100 °C for 10 min followed with release (10 °C/ min up to 600 °C). (b) NO, C_3H_6 co-adsorption at 100 °C for 10 min followed with release (10 °C/min up to 600 °C).

Table 2

Storage features of NO and $C_{3}H_{6}$ and amount of released CO over Pd/SSZ-13.

Catalyst	NO only adsorption		NO +	C ₃ H ₆ co-ac	sorption Released CO ^c (μmol/ g·catalyst)	
	NSC ^a	NO _x / Pd ^b _{total}	NSC	NO _x / Pd _{total}	208–306 °C	306–413 °C
2 Pd	96	0.51	122	0.65	37.2	39.4

 aNO_x storage capacity (µmol/g-catalyst), obtained from NO storage content in NO uptake at 100 °C;

^bMolar ratio of stored NO_x to Pd_{total}

^cObtained from the results shown in Fig. 4b.

To further analyze the nature of Pd species and SSZ-13, the different as-prepared Pd/SSZ-13 catalysts (after calcination at 650 °C in air for 5 h) were characterized by XRD, as shown in Fig. 2. H-SSZ-13 showed a typical CHA structure [6]. The diffraction peaks of the 2 Pd catalyst were more or less identical to those of H-SSZ-13. No other diffraction peaks belonging to PdO ($2\theta = 33.9^{\circ}$) or Pd ($2\theta = 40.1^{\circ}$) [28,56] were detected, demonstrating that any non-exchanged Pd species, if present, should be highly dispersed in SSZ-13.

Fig. 3 shows the TEM image of the 2 Pd sample. Rather uniformly and highly dispersed Pd particles were observed for all catalysts, as shown in Fig. 3a. Since the catalysts were imaged after calcination at 650 °C in air, these particles should be PdO species. Bringing the TEM data into context with the results from XRD and N₂ physical adsorption, one can conclude that the PdO particles should mainly be formed and located within the SSZ-13 cages [57].

3.2. Performance of NO_x (C₃H₆) adsorption and release on Pd/SSZ-13

3.2.1. NO adsorption in absence of C_3H_6

Fig. 4a shows the profiles of NO_x (including NO and NO_2) concentration versus time on stream in the continuous reaction gas feed, which consisted of by-pass feed (10 min), followed by NO storage (at 100 °C for 10 min) and subsequent release under the same gas feed conditions during the temperature ramp (10 °C/min up to 600 °C) over Pd/SSZ-13. Since the NO inlet concentration was 200 ppm, negative peaks below the 200 ppm baseline reflect the storage or adsorption of NO, and positive peaks above 200 ppm indicate the release or desorption. After switching the feed gases from by-pass to the catalyst, negative NO adsorption peaks were observed. The NO_x profiles almost coincided with the NO curves except for some NO_2 observed at 100 °C. On H-SSZ-13 at 100 °C (Fig. S4) no detectable NO adsorption and oxidation to NO_2 occurred.

The integrated area of the negative peak for NO_x adsorption and the corresponding results for NO_x storage characteristics on 2 Pd are shown in Table 2. A NO_x/Pd mole ratio of 0.51 was achieved during NO uptake at 100 $^{\circ}$ C.

3.2.2. Simultaneous NO and C₃H₆ adsorption

Fig. 4b presents the concentrations profiles versus the time on stream for NO + C_3H_6 co-adsorption and release over the Pd/SSZ-13 catalysts. Negative peaks due to NO adsorption were observed at 100 °C. But the small NO₂ peak, which was observed during NO only adsorption, was not observed during NO storage in the presence of C_3H_6 at 100 °C, which indicates that NO is the primary storage species and the formation of NO₂ is inhibited when C_3H_6 is in the feed during NO adsorption. Table 2 shows that the amounts of stored NO at 100 °C were slightly enhanced when C_3H_6 was co-adsorbed than when C_3H_6 was absent in the feed.

Concurrently with NO adsorption in the presence of C_3H_6 at 100 °C, negative C_3H_6 storage peaks were also observed for all catalysts. As the adsorption of C_3H_6 was undetectable on H-SSZ-13, the adsorption of C_3H_6 must be related to the presence of Pd sites in Pd/SSZ-13 (Fig. S4).

3.2.3. Release characteristics after NO storage in absence of C_3H_6

After NO adsorption at 100 °C, the release of stored NO in the same reactive gas feed occurred when the temperature increased from 100 to 600 °C, as shown in Fig. 4a. A strong re-adsorption of NO was observed immediately after the sample temperature increased to 100–200 °C. Meanwhile, a big NO₂ desorption peak was observed at 186 °C. The net impact (shown in Fig. 4a) was the formation of a small negative peak of NO_x at 186 °C. This second NO adsorption with NO₂ formation was previously attributed to the NO adsorption on reduced Pd ions, following the pathway below [33].

 $3 \text{ NO} + 2 \text{ Z-Pd}(\text{OH})^+ = 2 \text{ Z-Pd} + -\text{NO} + \text{NO}_2 + \text{H}_2\text{O} (1).$

In the temperature range of 210–450 °C, a large and broad NO_x release peak was observed, and the release profile of NO was coincident with that of NO_x but no NO₂ peak was observed. At the release temperature above 450 °C, NO_x was maintained at the feed concentration of 200 ppm, while the concentration of NO decreased to less than 200 ppm as part of the NO was oxidized to NO₂ that was immediately detected in the flow. This indicates that the catalytic oxidation of NO to NO₂ occurred over Pd/SSZ-13 above 450 °C [21].

3.2.4. Release characteristics after simultaneous $NO + C_3H_6$ co-adsorption

The release behavior after NO + C₃H₆ co-adsorption showed remarkably different characteristics from those without C3H6 in the feed, as shown in Fig. 4b. Generally, for the entire course, unlike the results shown in Fig. 4a, NO2 release peaks were not observed except catalytic oxidation of gaseous NO to NO2 at temperatures above 485 °C. Therefore, the release profiles of NO_x exactly resembled the curves of NO release in the range of 100-485 °C. In the range of 100-200 °C, the readsorption of NO still occurred as a small negative NO peak at 185 °C was observed, but the NO2 peak was not observed in this case. This indicates that the presence of C₃H₆ inhibited the NO₂ formation. It is known that the NO₂ has strong oxidizing capacity, which can easily react with C₃H₆ [58]. While the C₃H₆ concentration is even a little higher than 200 ppm at 186 °C. This demonstrates that reduction of NO₂ by C₃H₆ did not occur, otherwise the C3H6 would be consumed, and the concentration would be lower. Therefore, it is likely that the presence of C_3H_6 suppressed the Pd ions reduction by NO in Eq. (1) in the second NO uptake (186 °C).

In the range of 200–485 °C, a NO release peak (T = 275 °C) was immediately followed by a re-adsorption peak (T = 328 °C) in the range of 300–338 °C, which was then followed by a large and dominant release peak (T = 423 °C) in the temperature range 338–485 °C. At temperatures above 485 °C, similar to the case of NO only, NO_x was maintained at the feed concentration of 200 ppm whereas the concentration of NO dropped below 200 ppm (Fig. 4b) due to the formation of NO₂ by the catalytic oxidation of NO [21]. This indicates that the catalytic oxidation of NO to NO₂ over Pd/SSZ-13 above 485 °C was not affected by C₃H₆.

For the case of C_3H_6 release in the entire temperature range from 100 to 600 °C, no apparent concentration increase due to C_3H_6 desorption was observed. On the contrary, the C_3H_6 concentration in the stream started to decrease at 197 °C, reaching 100 % removal of C_3H_6 at 303 °C. This indicates that both C_3H_6 pre-adsorbed at 100 °C and C_3H_6 in the feed were oxidized over Pd/SSZ-13 during the course of release. Furthermore, two peaks of CO formation were observed during the course where the C_3H_6 concentration decreased. The first peak was in the temperature range of 208–306 °C. The second peak of CO formation occurred after the complete removal of C_3H_6 in the stream, in the range of 306–413 °C with the peak at 336 °C. The formation of CO must be attributed to the catalytic oxidation of C_3H_6 over Pd/SSZ-13.

3.3. Oxidation characteristics of Pd/SSZ-13

Complex chemistry occurs during $NO + C_3H_6$ release, including C_3H_6 oxidation with formation of CO as an intermediate, NO release, NO



Fig. 5. Light-off curves of CO (a) and C_3H_6 (b) oxidation over Pd/SSZ-13 catalysts. Reaction conditions: 200 ppm CO (C_3H_6), 10 % O_2 , 5 % H_2O , 5 % CO_2 and balanced with N_2 ; the light-off runs started from 100 °C with a ramping rate of 2 °C/min. All the reactions were kept at WHSV = 600, 000 mL g⁻¹h⁻¹.



Fig. 6. Steady-state C_3H_6 oxidation over 2 Pd sample in different conditions. The procedures are shown in the bottom. 50 mg of catalysts were used, and the flow rate was 250 mL/min.

oxidation to NO₂, etc. To elucidate the chemistry in NO + C_3H_6 releases in Fig. 4b, separate oxidation experiments were carried out to investigate the characteristics of CO and C_3H_6 oxidation over Pd/SSZ-13.

3.3.1. CO and C_3H_6 oxidation

Fig. 5a shows light-off curves of CO oxidation under the simulated conditions (10 % O₂-5 % H₂O-5 % CO₂) over the Pd/SSZ-13 catalysts. T₅₀ (the temperature of 50 % conversion), which is representative of light-off, was 153 °C for 2 Pd. Furthermore, T₁₀₀, which is used for the comparison of catalytic ability for complete CO oxidation, was 170 °C for 2 Pd. The values for T₅₀ and T₁₀₀ indicate that 2 Pd is highly active on CO oxidation.

Fig. 5b shows the results of C_3H_6 oxidation over the Pd/SSZ-13 catalysts. The light-off curves showed that the T_{50} was 245 °C whereas the T_{100} was 285 °C for the 2 Pd. The CO formation peak (in the range of

200–300 °C) was at 250 °C, where the 100 % C_3H_6 conversion was not achieved. This indicates that CO formation can be attributed to the incomplete oxidation of $C_3H_6.$

3.3.2. Steady-state catalytic C₃H₆ oxidation with NO on Pd/SSZ-13

It is known that NO has a significant impact on C_3H_6 oxidation [2]. To clarify the effect of NO on C₃H₆ oxidation over Pd/SSZ-13, steady state C₃H₆ oxidation with and without NO in the feed was investigated. The procedure and the corresponding curves are shown in Fig. 6. In the absence of NO, the C_3H_6 conversion at 230 °C was 85 % for 2 Pd. However, the C₃H₆ concentration increased to some extent after introducing NO into the feed, indicating that NO inhibits C₃H₆ oxidation. This inhibition was very significant at 230 °C and 260 °C over 2 Pd catalyst. Such an inhibitory role is consistent with the previous study [2], where C_3H_6 oxidation activity over $C_{03}O_4$ was suppressed by NO. The inhibitory effect of NO is most likely related to the formation of nitrate species on the catalyst surface by competitive adsorption of NO and C₃H₆. This hypothesis can be confirmed by the FTIR spectra shown in Fig. S5, where $C_{3}H_{6}$ oxidation intermediates (1457 and 1510 cm⁻¹ for ν_s (COO) and ν (C=C) in π -C₃H₅, respectively) were accompanied by a small amount of nitrates (1550-1684 cm⁻¹) formed on 2 Pd under cofeeding of C_3H_6 and NO in 20 % O_2/N_2 at 200 °C [16,59].

Pd supported on zeolite is an effective catalyst for the selective catalytic reduction of NO to N₂ by HCs [60,61]. However, at any temperature stage in Fig. 6, the NO_x concentration remained unchanged at 200 ppm, therefore, the reduction of NO_x by C_3H_6 over the Pd/SSZ-13 catalysts can be clearly ruled out. This might be attributed to the low capacity of Pd/SSZ-13 on NO oxidation to NO₂ which is believed as a preliminary step of the overall reduction of NO in C_3H_6 -SCR [21,62].

3.4. Fractional $C_{3}H_{6}$ (NO) adsorption and temperature-programmed oxidation

Clearly, NO_x release profiles were different in the presence of C_3H_6 (Fig. 4). During the release, C_3H_6 can come from two sources: one is the C_3H_6 that has been pre-adsorbed at 100 °C, and the second source is the feed. To investigate the effect of pre-adsorbed C_3H_6 on the NO_x release over Pd/SSZ-13, a series of the pre-adsorption/release experiments were conducted. It should be pointed that in each test the base gases (5 % H₂O and 5 % CO₂) were always present.

 C_3H_6 adsorption/temperature-programmed oxidation (TPO) was carried out to measure the oxidation of pre-adsorbed C_3H_6 during release, as shown in Fig. 7a. After exposure of C_3H_6 to 2 Pd, a strong negative C_3H_6 adsorption peak was observed. Then the C_3H_6 feed was switched to O_2/N_2 flow to purge the catalyst for 30 min, which was



Fig. 7. (a) C_3H_6 adsorption at 100 °C for 30 min followed with TPO (10 °C/min up to 600 °C). Reaction condition: 200 ppm of C_3H_6 (during adsorption), 10 % O_2 , 5 % H_2O , 5 % CO_2 , balanced with N_2 (b) NO, C_3H_6 co-adsorption at 100 °C for 10 min followed with TPO (10 °C/min up to 600 °C). Reaction conditions: 200 ppm of NO (during adsorption), 200 ppm C_3H_6 (during adsorption), 10 % O_2 , 5 % H_2O , 5 % CO_2 , balanced with N_2 . (c) NO, C_3H_6 co-adsorption at 100 °C for 10 min followed with TPD in NO (10 °C/min up to 600 °C). Reaction conditions: 200 ppm of NO, 200 ppm C_3H_6 (during adsorption), 10 % O_2 , 5 % CO_2 , balanced with N_2 . (c) NO, C_3H_6 co-adsorption at 100 °C for 10 min followed with TPD in NO (10 °C/min up to 600 °C). Reaction conditions: 200 ppm of NO, 200 ppm C_3H_6 (during adsorption), 10 % O_2 , 5 % H_2O , 5 % CO_2 , balanced with N_2 . In each condition the flow rate of 250 mL/min and 50 mg of catalysts were applied.

followed by TPO from 100 to 600 °C. Small CO peak at 276 °C was observed over 2 Pd, and no C_3H_6 was detected during TPO. This indicates that the pre-adsorbed C_3H_6 was oxidized over 2 Pd during TPO.

Fig. 7b shows the C_3H_6 + NO co-adsorption and the subsequent TPO. Similar to the C₃H₆ adsorption/TPO in Fig. 7a, a CO peak at around 280 °C appeared for 2 Pd, and no C₃H₆ release was detected. Moreover, a broad NO release with a peak at 385 °C appeared. To further investigate the influence of pre-adsorbed C₃H₆ on NO release, C₃H₆ + NO was preadsorbed, but the release was performed with only NO in the feed during the period of release, as shown in Fig. 7c. After C₃H₆ + NO co-adsorption at 100 $^{\circ}$ C for 15 min, the catalyst was purged by NO + O₂ flow for 30 min prior to the temperature ramping to 600 °C for release. During the release, a CO desorption peak appeared at 323 °C for the 2 Pd, at temperatures higher than that (around 280 °C in Fig. 7b) for the release in the absence of NO. No C₃H₆ release peak was observed, indicating that the pre-adsorbed C₃H₆ was completely oxidized. The shift in the CO peak temperature from 280 to 323 °C can be attributed to the suppression of NO on the oxidation of pre-adsorbed C₃H₆, consistent with results in Fig. 6. In addition, the temperature of NO release was in the range of 328-485 °C, which is consistent with the second NO release peak (330-485 °C) in Fig. 4b.

3.5. Drifts for co-adsorption and release over Pd/SSZ-13

NO and HCs can be adsorbed on Pd^{2+} ions in Pd/zeolite forming stable intermediates [13,16,32,63]. To elucidate the characteristics of NO or NO + C₃H₆ adsorption and release on Pd/SSZ-13, a series of DRIFTs studies with different gas feed sequences were carried out. The changes in spectra with increasing temperature were also collected. To simulate the reaction conditions in Fig. 4, all IR spectra were recorded in the presence of 5 % H₂O.

3.5.1. Drifts for NO adsorption and release

Fig. 8a shows the NO adsorption/release spectra. Typically, in the previous works, two peaks at 1860 cm⁻¹ and 1810 cm⁻¹ appeared in the spectra of NO adsorption on Pd/zeolite in the absence of H₂O, which were assigned to the NO adsorption on Pd²⁺ and Pd⁺, respectively, on the basis of DFT calculation and experimental results [33,49,64]. While the presence of H₂O renders the assignment of IR peaks for NO adsorption on Pd/SSZ-13 rather complex, as the NO adsorption IR peaks on different state of Pd ions appear in a very close region with H₂O in feed [51,65,66], which is difficult to be clearly distinguished. For example, only IR peak at around 1810 cm⁻¹ remained after the exposure of H₂O, while 1860 cm⁻¹ peak was significantly decreased or disappeared [51,65,66]. Although the effect of multiple H₂O adsorption on Pd and H₂O solvation of Pd nitrosyl complexes is still not comprehensively understood, it can be certain that, with 5 % H₂O in feed, the water can easily access and coordinate to Pd sites to form H₂O solvated Pd ions at around 100 °C [51,65]. After the NO adsorption at 100 °C, only a small peak centered at 1810 cm⁻¹ was observed. Consequently, this IR peak can be ascribed to the NO adsorption on H2O-solvated Pd cations [13].

As the temperature increased to 200 °C, the intensity of band at 1810 cm⁻¹ increased, and a peak at 1858 cm⁻¹ appeared. The H₂O-solvated Pd ions would loss the H₂O as the temperature increased to 200 °C [33]. Therefore, the peaks at 1858 and 1810 cm⁻¹, in spectra collected at and above 200 °C, should be attributed to the Pd²⁺(NO) and Pd⁺(NO), respectively, as discussed at the beginning of this section.

As the temperature increased to 275 °C, the band at 1810 cm⁻¹ decreased, while the band at 1858 cm⁻¹ almost keep constant, suggesting that the NO in Pd⁺–NO shows a lower bonding strength than that in Pd²⁺(NO), consistent with the results reported by Liu *et al.* [38].

As the temperature increased to 336 °C, The $Pd^{2+}(NO)$ start to decompose and the less stable Pd^+ –NO was completely decomposed. It should be pointed that the threshold temperature for decomposition of $Pd^{2+}(NO)$ cannot be clearly determined here. Only a small peak at 1858

Fig. 8. In situ FTIR spectra of Pd/SSZ-13 catalyst (a) NO adsorption at 100 °C followed by temperature ramping in the same reactant gases. (b) NO + C_3H_6 adsorption at 100 °C followed by temperature ramping in the same reactant gases. n = 1, 2. The concentration of NO and C_3H_6 was kept at 1000 ppm. The spectra at 100 °C were collected after stabilization for 30 min. The ramping rate for release was 10 °C/min, consistent with that in Fig. 4.

cm⁻¹ was observed at 450 °C, revealing that the NO release (Fig. 4a) should be exclusively ascribed to the decomposition of $Pd^{2+}(NO)$ in 336–450 °C.

3.5.2. Drifts for NO + C_3H_6 co-adsorption and release

Fig. 8b shows the NO + C₃H₆ adsorption/release on Pd/SSZ-13. A dominate IR peak at 1703 $\rm cm^{-1}$ was observed upon NO $+ \ \rm C_3H_6$ adsorption at 100 °C. Fig. 4b and Fig. 7b show that both NO and C_3H_6 were adsorbed on Pd/SSZ-13 at 100 $^{\circ}\text{C}$ during NO + C_3H_6 co-adsorption (Fig. 4b). The results suggest that Pd^{2+} ions not only serve as storage sites for NO but also might be active for C_3H_6 adsorption. Therefore, the peak at 1703 cm⁻¹ might be attributed to the co-adsorption of C₃H₆ and NO on Pd ions. Previous work reported that the co-adsorption of C₃H₆ and NO would reduce Pd^{2+} to Pd^+ forming Pd^+ -NC₃H₆O complex in Pd/ Beta, supported by formation of acetone during reactant uptake [38]. However, no oxidation products of C₃H₆, such as acetone or acetaldehyde, were observed in $NO + C_3H_6$ co-adsorption on 2 Pd; in addition, the results in Fig. 7a and Fig. 7b indicate that the C₃H₆ was stored rather than oxidized on 2 Pd during uptake period at 100 °C. This rules out the possibility of reduction of Pd^{2+} by oxidizing C_3H_6 at 100 °C. In a previous work by Khivantsev et al. [49], the IR peak for NO adsorption on Pd ions (1866 cm⁻¹) shifted to 1774 cm⁻¹ after the exposure of C₂H₄, which was assigned to $Pd^{2+}(NO)(C_2H_4)$ complex. Therefore, analogous

to the $Pd^{2+}(NO)(C_2H_4)$, the peak formed in 1703 cm⁻¹ (1765 cm⁻¹ in the absence of H₂O, Fig. S9), formed in NO + C₃H₆ co-adsorption on Pd/SSZ-13, can be attributed to $Pd^{2+}(NO)(C_3H_6)$ complex.

As the temperature increased from 100 to 275 °C, the bands at 1811 and 1853 cm⁻¹ increased at the expense of band at 1703 cm⁻¹. This result demonstrates the transformation of $Pd^{2+}(NO)(C_3H_6)$ to $Pd^{2+}(NO)$ and $Pd^{+}(NO)$ complex in 100–275 °C.

As the temperature increased to 336 °C, no changes were observed in peak at 1811 cm⁻¹ and the band at 1853 cm⁻¹ increased at 336 °C shown in Fig. 8b; at the same time, the band at 1703 cm⁻¹ disappeared. This is different with the observation that the bands at 1810 cm⁻¹ and 1858 cm⁻¹ decreased as the temperature increased from 275 to 336 °C in Fig. 8a. Since both Pd²⁺(NO) and Pd⁺(NO) would be decomposed at a temperature of 275–336 °C (Fig. 8a), the lack of change/increment of bands at 1811/1853 cm⁻¹ (Fig. 8b) should be attributed to the continuous transformation of Pd²⁺(NO)(C₃H₆) to Pd²⁺(NO) and Pd⁺(NO).

As the temperature increased to 450 °C, the band at 1853 cm⁻¹ decreased and the band at 1811 cm⁻¹ almost disappeared, indicating that the NO release at temperatures of 336–450 °C is attributed to the decomposition of $Pd^{2+}(NO)$ and $Pd^{+}(NO)$. Since only a dominant peak at 1853 cm⁻¹ was observed in the IR spectrum at 450 °C, the decomposition of $Pd^{2+}(NO)$ contributes to the NO release above 450 °C.

4. Discussion

4.1. The enhancement of NO adsorption by C_3H_6 at 100 °C

It has been reported that NO uptake on Pd ions in Pd/SSZ-13 is strongly suppressed in the presence of H₂O at 100 °C. This can be attributed to the H₂O solvated effect on Pd²⁺ make it difficult for the NO molecules to coordinate at 100 °C [16,33].

The enhancement of NO storage capacity by the co-feed of C_3H_6 at 100 °C was observed compared to the result of NO only adsorption on Pd/SSZ-13 (shown in Table 2). Therefore, the enhanced NO storage capacity of Pd/SSZ-13 should be related to the presence of C_3H_6 . Different from that of NO adsorption alone, both NO and C_3H_6 were adsorbed on Pd/SSZ-13 at 100 °C during NO + C_3H_6 co-adsorption (Fig. 4b), ascribed to the simultaneous adsorption of C_3H_6 and NO on Pd²⁺ ions forming a Pd²⁺(NO)(C₃H₆) complex (Fig. 8b). Furthermore, the formation of the Pd²⁺(NO)(C₃H₆) complex was not affected by H₂O, as the IR spectra were similar in C_3H_6 + NO co-adsorption regardless of whether H₂O was present in the feed (Fig. S9). These observations indicate that the hydrolysis of Pd cations was impeded by C_3H_6 at 100 °C, due to the formation of Pd²⁺(NO)(C₃H₆), which improves the NO adsorption capacity of 2 Pd.

4.2. Effect of C_3H_6 on NO release characteristics

4.2.1. C_3H_6 oxidation during release

Both pre-adsorbed C₃H₆ and C₃H₆ in the feed were oxidized over Pd/ SSZ-13 during the release in NO + C₃H₆ co-adsorption, and CO was formed as one of the products during C₃H₆ oxidation. Two CO peaks were observed during the course of release (Fig. 4b). The temperature window of the first CO peak falls in the temperature range (200-300 °C) of less than 100 % C3H6 conversion. Similar CO formation peaks were also observed in the C₃H₆-only oxidation when the C₃H₆ conversion was less than 100 % (Fig. 5b). This indicates that the CO formation peak in the 200-300 °C range during release (Fig. 4b) should be due to the incomplete oxidation of C3H6 in the feed. The second CO peak was broad and in the temperature range of 300–410 $^{\circ}$ C (Fig. 4b), where C₃H₆ in the feed was completely converted, which could rule out the possibility that CO formation in this temperature range is ascribed to the incomplete oxidation of C₃H₆ from the gaseous feed. As a similar CO release peak at 323 $^\circ\text{C}$ was observed in Fig. 7c when NO + C_3H_6 was co-adsorbed and then the release was performed in the $NO + O_2$ environment, the second CO formation peak in Fig. 4b should be attributed to the oxidation of pre-adsorbed C_3H_6 on the Pd^{2+} ions sites.

2 Pd contains both PdO and Pd²⁺ ions (Fig. 1 and Fig. 3). IR results show that most of Pd ions did not change as $Pd^{2+}(NO)(C_3H_6)$ in 200–275 °C (Fig. 8b), indicating the Pd²⁺ should not be responsible for the oxidation of C₃H₆ in feed. Therefore, it is likely that PdO sites catalyzed the oxidation of gaseous C3H6 with the formation of CO intermediates as the temperature increased from 200 °C to 275 °C. There is some $Pd^{2+}(NO)(C_{3}H_{6})$ ions were transformed to $Pd^{+}(NO)$ during oxidation of pre-adsorbed C₃H₆ in 275-336 °C (Fig. 8b). This implies that Pd^{2+} ions are active in the oxidation of pre-adsorbed C_3H_6 in $Pd^{2+}(NO)(C_3H_6)$ during release period, which reduces Pd^{2+} to Pd^+ . However, not all the pre-adsorbed C_3H_6 was oxidized over \mbox{Pd}^{2+} ions in 275–336 °C, as $Pd^{2+}(NO)$ complex was also formed after the C_3H_6 oxidation in $Pd^{2+}(NO)(C_3H_6)$ (Fig. 8b). This demonstrates that PdO sites were also taking part in the oxidation of pre-adsorbed C₃H₆ on Pd²⁺ ions. The distances between $Pd^{2+}(NO)(C_3H_6)$ and PdO might determine the C3H6 oxidation pathway, which means that the close distance between Pd^{2+} ions and PdO might facilitate the diffusion of C_3H_6 from Pd^{2+} to PdO for oxidation to form $Pd^{2+}(NO)$.

The incomplete oxidation of C_3H_6 to CO is a typical phenomenon when the ratio of C_3H_6 to oxygen is less than the stoichiometric ratio of oxygen required for complete oxidation of C_3H_6 to CO₂ [67]. However, in the present work, the oxygen concentration (10 %) is much higher than the stoichiometric ratio for the complete oxidation of C_3H_6 (0.09 %). The formation of CO indicates that the oxygen in the feed is not a controlling factor in the C_3H_6 oxidation over Pd/SSZ-13 catalysts. A similar incomplete C_3H_6 oxidation to CO over Pd/Al₂O₃ with excess oxygen was also observed by Hazlett *et al.* [68], who found that CO was formed when the C_3H_6 conversion was less than 100 %. They proposed that stronger adsorption of C_3H_6 than oxygen over Pd sites on Pd/Al₂O₃ catalyst restricts the dissociation and activation of oxygen, resulting in the incomplete oxidation of C_3H_6 [69,70]. It is likely that the suppressed activation of oxygen over the Pd sites results in the incomplete oxidation of C_3H_6 to CO over 2 Pd.

4.2.2. The NO release affected by C_3H_6 and intermediate CO

The NO release differs in temperature ranges after only NO adsorption/release in NO flow (200–450 °C, Fig. 4a) and C_3H_6 + NO coadsorption/release in NO flow (330-475 °C, Fig. 7c). This indicates that the pre-adsorbed C_3H_6 on Pd^{2+} ions increased the NO release temperature. The results of DRIFTs in Fig. 8 show that NO gets stored as $Pd^{n+}(NO)$ (n = 1, 2) or $Pd^{2+}(NO)(C_3H_6)$ without or with C_3H_6 , respectively. Therefore, the released NO in Fig. 4a should be attributed to the NO dissociation from $Pd^{n+}(NO)$, but the NO release in Fig. 7c should be due to the NO dissociation from $Pd^{2+}(NO)(C_3H_6)$. The different NO release temperatures in Fig. 4a and Fig. 7c should be attributed to the different thermal stabilities of Pdⁿ⁺(NO) and Pd²⁺(NO)(C₃H₆) complexes. Pd⁺(NO) and Pd²⁺(NO) start to decompose as the temperature increased from 200 to 275 °C and from 275 to 336 °C, respectively (Fig. 7a), contributing to the NO release in 200-450 °C in NO adsorption/release in NO flow (Fig. 4a). The NO release in Fig. 7c occurred only after the oxidation of C_3H_6 in $Pd^{2+}(NO)(C_3H_6)$ which was completely transformed to Pdⁿ⁺(NO) above 328 °C (Fig. 8b). This result demonstrates that the Pd²⁺(NO)(C₃H₆) is much more thermal stable than $Pd^{2+}(NO)$ and $Pd^{+}(NO)$ (Fig. S14), and the shielding effect of C_3H_6 improved NO release temperature in NO + C₃H₆ co-adsorption/release in NO flow in Fig. 7c.

In comparison to the result in Fig. 7c, another NO release peak in the range of 210–300 °C was observed in Fig. 4b when C_3H_6 was present in the feed during release. This clearly indicates that $Pd^{2+}(NO)(C_3H_6)$ was transformed to other complexes with lower thermal stability due to the presence of C_3H_6 in the feed; otherwise, the NO release temperature should be above 328 °C (Fig. 7c). DRIFTs results (Fig. 8b) show that $Pd^{n+}(NO)$ increased at the expense of $Pd^{2+}(NO)(C_3H_6)$ as the temperature increased from 200 to 336 °C, demonstrating that the presence of C_3H_6 in feed during release promotes the conversion of $Pd^{2+}(NO)(C_3H_6)$ to $Pd^{n+}(NO)$ (n = 1, 2). Thereafter, this promotional effect is analyzed.

The C₃H₆ in feed was oxidized on 2 Pd and CO was formed as an intermediate (Fig. 4b) in the temperature of 200-300 °C. It should be noted that the NO release profile in Fig. 4b shows a typical volcanoshaped curve in the range of 210-300 °C with the changes of concentration of detectable CO in the stream. Within the 200-275 °C temperature range, the NO concentration increased with increasing temperature, while the concentration of CO in the stream also increased. In contrast, the NO concentration decreased with further increasing temperature from 275 to 300 $^{\circ}$ C, where the CO concentration from C₃H₆ oxidation decreased. After C3H6 in the stream was totally converted at 300 °C, NO release was stopped. The above results suggest that the transformation of Pd²⁺(NO)(C₃H₆) to Pdⁿ⁺(NO) in 200–275 °C is closely related to the concentrations of CO in the stream. The FTIR results (Fig. S11) demonstrate that the presence of CO facilitates the transformation of Pd²⁺(NO)(C₃H₆) to Pd²⁺(NO)(CO), as CO can displace C_3H_6 in Pd²⁺(NO)(C₃H₆). Furthermore, the Pd²⁺(NO)(CO) complex is not stable, and can be easily decomposed to $Pd^{n+}(NO)$ at temperatures above 200 °C (Fig. S13) [71]. Consequently, the CO formation due to oxidation of C₃H₆ in the feed facilitates the transformation of thermally stable $Pd^{2+}(NO)(C_{3}H_{6})$ to $Pd^{2+}(NO)(CO)$ which would be subsequently converted to $Pd^{n+}(NO)$, and NO dissociation from $Pd^{n+}(NO)$ results in NO release in the range 210-300 °C (Fig. 5b).

- $Pd^{2+}(C_3H_6)(NO) + 3O_2 \rightarrow Pd^{n+}(NO) + 3CO + 3H_2O$
- $Pd^+ + O_2 \rightarrow Pd^{2+}$
- $Pd^{2+} + NO \rightarrow Pd^{2+}(NO)$

Fig. 9. The mechanistic scheme of simultaneous storage and release of NO and C_3H_6 on the Pd/SSZ-13 catalyst.

A NO re-adsorption peak appeared as the temperature increased from 300 to 345 °C in Fig. 4b but was not observed in Fig. 4a. Since only the Pd^{*n*+} ions are NO adsorption sites [13,16,29], the re-adsorption of NO should be related to unoccupied Pd^{*n*+} after NO desorption at 210–300 °C. The Pd⁺–NO and Pd²⁺–NO decompose in the temperature range of 200–275 °C and 275–336 °C, respectively (Fig. 8a). Therefore, NO re-adsorption cannot occur on Pd⁺ at 300–345 °C, due to the low stability of Pd⁺–NO (Fig. 8a); thus, the re-adsorption should occur on Pd²⁺ ion sites. Furthermore, the re-adsorption of NO on Pd²⁺ ions (300–345 °C) demonstrates that the NO did not dissociate from Pd²⁺(NO) below 300 °C. Therefore, the NO release in 210–300 °C in Fig. 4b is primarily attributed to the NO dissociation from Pd⁺–NO. It is likely that some unoccupied Pd⁺ ions, formed after NO desorption at 210–300 °C, were oxidized to Pd²⁺, which adsorbed NO and contributed to the NO re-adsorption peak in 300–345 °C (Fig. 4b).

In addition, the oxidation of Pd⁺ to Pd²⁺ by O₂ is only occurred above 275 °C [35], indicating that the oxidation of Pd⁺ requires high energy. In the same work, it was also found that the oxidizing capacity of the feed gas would affect the Pd⁺ oxidation: the more reducing the gaseous mixture, the more difficult for Pd⁺ oxidation [35]. The presence of reduction gases (C₃H₆) should inhibit the oxidation of Pd⁺ to Pd²⁺. Therefore, the Pd⁺ oxidation to Pd²⁺ in Fig. 4b must occur above 275 °C (Fig. 4b). In addition, the Pd²⁺(NO) would decompose above 336 °C (Fig. 8a). Therefore, the re-adsorption caused by Pd⁺ oxidation to Pd²⁺ was only observed in 275–336 °C in Fig. 4b.

With increasing temperature to above 345 °C, C_3H_6 in $Pd^{2+}(NO)$ (C_3H_6) was completely oxidized forming $Pd^{n+}(NO)$ (Fig. 8b). The NO dissociation in $Pd^{n+}(NO)$ resulted in the second NO release peak (Fig. 4b). Combining all the results and the discussion above, the mechanistic pathways of the NO + C_3H_6 co-adoption and release have been summarized in Fig. 9.

5. Conclusions

The Pd/SSZ-13 catalyst was prepared by the incipient wetness method and applied to NO storage by simultaneous NO + C_3H_6 coadsorption at a low temperature (100 °C) and release under simulated operation conditions. Pd²⁺ ions and PdO were identified. The Pd ions store NO, but can also serve as the storage sites for C_3H_6 at 100 °C. The co-existence of C_3H_6 enhances the NO storage capacity at 100 °C, which benefits from the simultaneous storage of NO and C_3H_6 in Pd/SSZ-13 by forming the Pd²⁺(NO)(C₃H₆) complex. PdO particles, which are highly dispersed in the pores of SSZ-13, are the active sites to catalytically oxidize both pre-absorbed C_3H_6 on Pd²⁺ ions and the C_3H_6 in feed. Pd²⁺ might only active on oxidizing the C_3H_6 in Pd²⁺(NO)(C₃H₆) complex.

Different NO release characteristics were observed after NO adsorption alone and NO + C_3H_6 co-adsorption. Only one broad NO release peak was observed in NO only adsorption, while two NO release peaks and a NO re-adsorption peak appeared after NO + C_3H_6 co-adsorption. Our adsorption/release experiments with different protocols and the results of DRIFTs suggest that the oxidation of C_3H_6 in feed to CO facilitates the transformation of $Pd^{2+}(NO)(C_3H_6)$ to $Pd^{n+}(NO)$ in 210–300 °C. The decomposition of Pd^{+} –NO contributes to the NO release in 210–300 °C. The oxidation of Pd^{+} to Pd^{2+} results in the NO re-adsorption at 300–345 °C. The oxidation of C_3H_6 in $Pd^{2+}(NO)$ (C_3H_6) which transforms to $Pd^{n+}(NO)$ is responsible for the second NO release peak above 345 °C.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2022.139507.

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