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Nitric oxide adsorption and desorption on alumina supported palladium

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Abstract

The adsorption properties of nitric oxide (NO) on alumina supported palladium were studied by a simultaneous thermogravimetric-analysis and differential-scanning-calorimetry (TGA-DSC) in a temperature ranges between 220 and 470 K. Upon adsorption, NO molecules on both Pd/Al_2O_3 and $Pd/NaOH\text{-}Al_2O_3$ samples were molecularly adsorbed between 220 and 300 K. Some NO molecules were strongly adsorbed on $Pd/NaOH\text{-}Al_2O_3$ and possessed a higher enthalpy of adsorption [$\sim$140 kJ (mol NO)$^{-1}$] than Pd/Al_2O_3 [$\sim$114 kJ (mol NO)$^{-1}$]. Upon heating above 320 K, the adsorbed NO molecule on these palladium surface was dissociated. In addition, a temperature programmed desorption and mass spectrometer (TPD–MS) study in a temperature range between 300 and 1100 K further indicated that some strongly adsorbed NO molecules may stay on basic sites ($*_b$) and Pd–NaOH interface sites ($*_i$) to enhance the decomposition of NO. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nitric oxide; Palladium; Calorimetry; Heat of adsorption; Adsorption

1. Introduction

Thermal properties of nitric oxide (NO) on transition metals have received considerable interest due to its importance for air pollution control [1,2]. The reduction of NO pollutants is one of the key research projects in the protection of our environment and new methods are being developed in many countries today [3]. While many techniques for surface analysis of NO adsorption and desorption on catalytic metals have been carried out using metal single crystals [4–11], but few investigations using supported catalysts [12–15]. Most industrial practical catalysts for NO removal consists of nanoscales metal particles dispersed on a

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high surface area oxide supports (typically 100–200 m^2/g) under atmospheric conditions. Among these catalysts, Pd/Al_2O_3 has been recognized very active in catalytic decomposition of NO in an oxidized environment at $T > 800$ K [16–18]. However, the adsorption and thermal behavior of NO on alumina supported palladium catalysts have not been well studied.

It therefore becomes an attractive research goal for alumina supported palladium catalysts. This study is concerned with the thermal behavior of NO adsorption, desorption and decomposition on alumina supported palladium surfaces. In particular, the influence of modified supports of the NaOH-coated alumina on the thermal desorption of NO is investigated.

2. Experimental

2.1. Sample preparation

Pd/Al_2O_3 catalysts of various palladium loadings were prepared by impregnating γ-Al_2O_3 (Merck, surface area: 108 m^2/g) with different amounts of an aqueous H_2PdCl_4 solution. Obtained slurries were pretreated sequentially with an overnight drying at 380 K and a 4 h calcination at 770 K before storing as testing sample.

Different NaOH-coated loadings (in wt.%) were impregnated on γ-Al_2O_3 support to prepare NaOH-Al_2O_3 supports. After a 4 h calcination at 900 K, part of the NaOH-Al_2O_3 support was subsequently impregnated with different amounts of an aqueous H_2PdCl_4 solution to prepare Pd/NaOH-Al_2O_3 catalysts. The dispersion (D, percentage of atoms exposed to surface) of palladium crystallites was estimated from hydrogen chemisorption isotherms performed in a volumetric system at 300 K. Table 1 lists dispersion estimated for all prepared samples.

2.2. Adsorption measurement

The amounts of NO uptake and heats evolved were monitored in a dual port calorimeter (Setaram TG-DSC 111) equipped with a sensitive balance (0.25 μg) and calorimeter (10 μW), respectively. A detailed description of this system had been given in the previous reported [19]. A single medium support (γ-Al_2O_3 or NaOH-Al_2O_3) was mounted in the reference port as a blank. Before the adsorption measurement, each testing sample was pre-reduced in flowing hydrogen gas at 570 K for 1 h and a subsequent evacuation (by evacuating to a vacuum of ca. 2×10^{-1} Torr) for 2 h at 720 K to desorb hydrogen adsorbate and, then, cooled back to 300 K for measurements of NO adsorption.

2.3. Temperature programmed desorption (TPD)

The thermal behavior of NO experiments was carried out on a temperature programmed desorption and mass spectrometer (TPD–MS) apparatus. The samples adsorbed NO at 300 K for 1 h in a flow reactor by NO feed gas (4% v/v of NO in He) then swept with He at a rate of 30 ml/min until the residual un-adsorbed NO purged out. Finally, the sample was heated

Table 1
Gas uptakes of chemisorbed hydrogen and nitric oxide at 300 K[a]

Sample	Hydrogen chemisorption		Nitric oxide chemisorption		N_{NO}^{ad}/N_H^m
	$D(N_H^m/N_{Pd})$	d (nm)	N_{NO}^{ad}/N_{Pd}	$-\Delta H_{ad}$ kJ (mol NO)$^{-1}$	
Pd/Al_2O_3 catalysts					
12.8%Pd	0.11	10	0.07	118	0.64
10.1%Pd	0.14	7.9	0.08	115	0.57
4.8%Pd	0.15	7.3	0.10	120	0.67
1.9%Pd	0.18	6.1	0.12	114	0.67
4.7%Pd	0.21	5.2	0.13	115	0.62
2.0%Pd	0.25	4.4	0.19	120	0.76
2.8%Pd	0.30	3.7	0.17	118	0.57
1.1%Pd	0.52	2.1	0.36	115	0.69
1.1%Pd	0.80	1.4	0.48	103	0.60
0.6%Pd	0.91	1.2	0.48	106	0.53
				114 ± 6	0.63 ± 0.07
Pd/13%NaOH-Al_2O_3 catalysts					
4.8%Pd	0.12	9.2	0.12	141	1.0
2.5%Pd	0.18	6.1	0.22	140	1.2
1.9%Pd	0.20	5.5	0.25	138	1.3
Pd/16.4%NaOH-Al_2O_3 catalysts					
1.9%Pd	0.10	11	0.075	124	0.75
1.6%Pd	0.12	9.2	0.086	128	0.71
1.2%Pd	0.18	6.1	0.14	128	0.78
Pd/6.5%NaOH-Al_2O_3 catalysts					
1.9%Pd	0.08	14	0.045	126	0.56
1.8%Pd	0.10	11	0.064	129	0.64
0.7%Pd	0.16	6.9	0.11	130	0.69

[a] N_H^m: monolayer uptake of hydrogen atom from H_2 chemisorption at $P_{H_2} = 10$ Torr and $T = 300$ K; d: average diameter of palladium crystallites calculated from $1.1/(N_H^m/N_{Pd})$.

at a rate of 10 K/min in He from 300 to 1000 K for recording the TPD–MS spectra. The desobates were analyzed by a quadrupole mass spectrometer (MS).

3. Results and discussion

3.1. Heats of adsorption (ΔH_{ad}) of NO measurement

The uptake of NO by each Pd/Al_2O_3 (or Pd/NaOH-Al_2O_3) sample at 300 K is maintained for 1.5×10^3 s. A typical time profile of simultaneous TG/DSC measurement on 7.75 mg of the reduced 10.1% Pd/Al_2O_3 sample is shown in Fig. 1. The measurement indicates that the adsorption of NO is an exothermic reaction and accompanies with a gain in weight. The rate of adsorption and heats evolved for NO on palladium crystallites are slower and smaller than the previous reported for dioxygen adsorption on platinum group metals (Pd, Pt and Rh) [19–21]. After 1.5×10^3 s adsorption, a $\Delta m = 18.0$ μg and a $q_{ad} = -68.8$ mJ

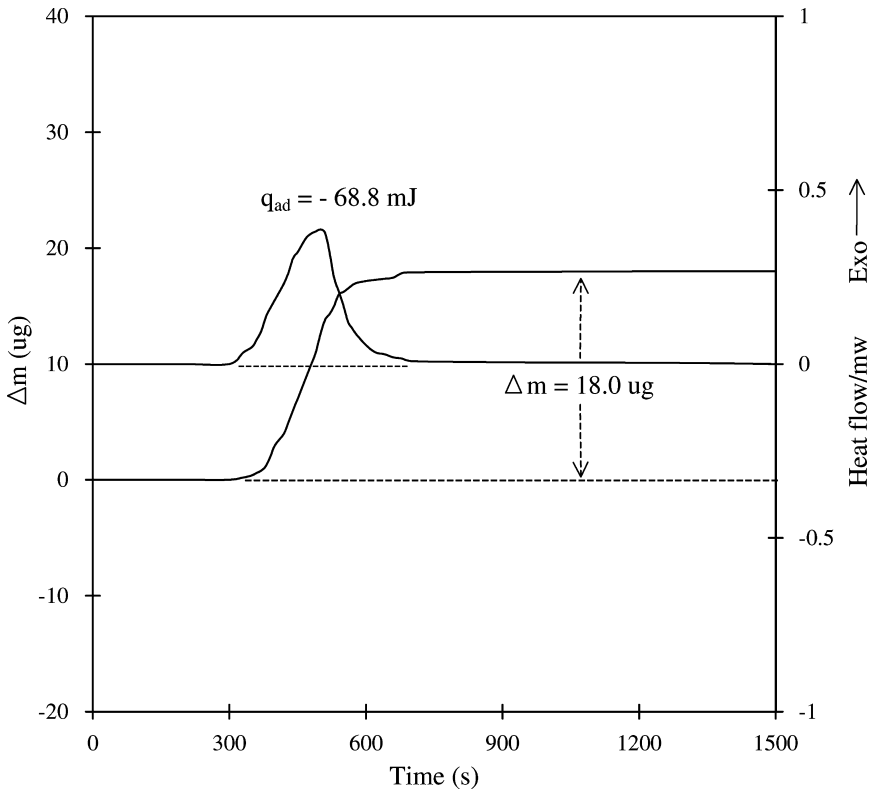

Fig. 1. A simultaneous TG-DSC measurement on adsorption of NO over a 7.75 mg 10.1%Pd/Al_2O_3 sample at 300 K.

are obtained. The NO uptake, N_{NO}, in each adsorption is determined according to the Δm obtained upon 1.5×10^3 s. Integral heats of adsorption, ΔH_{ad}, of NO on Pd/Al_2O_3 and Pd/NaOH-Al_2O_3 samples of different palladium dispersions measured at 300 K are listed in Table 1.

An apparent support effects and minor crystallite size effects on heat of adsorption of NO emerge in Table 1. Therefore, the enthalpy change of ΔH_{ad} and the stoichiometry for adsorption of NO, N_{NO}^{ad}/N_H^m, measured during TG-DSC are used comparatively for un-promoted Pd/Al_2O_3 and promoted Pd/NaOH-Al_2O_3 samples.

3.1.1. NO on Pd/Al_2O_3

As shown in Table 1, although the amounts of NO adsorption varies with both loading and the dispersion of palladium, a relatively constant stoichiometry of $N_{NO}^{ad}/N_H^m = 0.63 \pm 0.07$ and a constant enthalpy change of $-\Delta_{ad}H = 114 \pm 6$ kJ (mol NO)$^{-1}$ are obtained. The stoichiometry correlates sufficiently with ratio of 0.70 reported in the literatures for adsorption of NO on surface of various palladium single crystals [5–7,22,23]. As an indication of previously reported differential $-\Delta H_{ad}$ [7,22,24–28], as the NO surface coverage increased, $-\Delta H_{ad}$ decreasing gradually from 140 at initial adsorptions to 70 kJ (mol NO)$^{-1}$

at monolayer adsorptions. Therefore, the measured integral $-\Delta H_{ad}$ of 114 kJ (mol NO)$^{-1}$ listed in Table 1 for Pd/Al_2O_3 samples are consistent with the average of these two values.

3.1.2. NO on Pd/NaOH-Al_2O_3

Compared to NO on Pd/Al_2O_3, NO adsorbed on NaOH-coated $Pd/NaOH\text{-}Al_2O_3$ undergoes a significant difference on both the ΔH_{ad} and the N_{NO}^{ad}/N_H^m stoichiometry. Both values increase on coated Pd/Al_2O_3 samples with different amounts of NaOH. As seen in Table 1, the highest $-\Delta H_{ad}$ [140 kJ (mol NO)$^{-1}$] and the largest stoichiometry ($N_{NO}^{ad}/N_H^m > 1.0$) are found from samples coated with 13% NaOH. Which not only increasing the strength of NO on palladium crystallite surfaces, but also increasing the stoichiometry of NO adsorbed. The promotion effect of NaOH coating may be ascribed to a formation of additional active sites at interface between palladium and NaOH modified support that can adsorb NO molecule strongly.

To understand the phenomena of NO adsorbed, the uptake of NO in a temperature range between 220 and 470 K is calorimetrically studied. Table 2 shows the heat enthalpy (Q) and the N_{NO}/N_{Pd} stoichiometry with temperature for both 4.8%Pd/Al_2O_3 and 4.8%Pd/13%NaOH-Al_2O_3 samples. An obvious change initiates at 370 K for both samples. In general, the $-Q$ increasing with temperature, but the N_{NO}/N_{Pd} ratio remains constant for 4.8%Pd/Al_2O_3 sample. Both $-Q$ and N_{NO}/N_{Pd} ratio are increasing with temperature for 4.8%Pd/13%NaOH-Al_2O_3 sample. These results indicate that NO is molecularly adsorbed between 220 and 300 K. Upon heating above 320 K, NO adsorbed on these palladium surfaces is dissociated, leaving dissociated oxygen atom deposit on palladium surfaces. The surface bound oxygen atoms on Pd/Al_2O_3 in this measured temperature range block the active sites toward NO adsorption that exhibits a constant N_{NO}/N_{Pd} ratio with temperature. Whereas, the surface bound oxygen atoms on $Pd/NaOH\text{-}Al_2O_3$ may be combined with the extra bound NO to form NO_2 and being removed to the basic sites that abruptly changes the N_{NO}/N_{Pd} ratio upon heating above 320 K. The increase in heat enthalpy with increasing temperature is not surprising, since the ΔH_{ad}(O) is larger than ΔH_{ad}(NO) [19]. The NO molecules have either desorbed or dissociated above 320 K. Also, the surface adsorbed oxygen atoms penetrate into the sublayer region further oxidize the bulk palladium that elevates the heat enthalpy [19].

Table 2
Variations of heat enthalpy and the N_{NO}/N_{Pd} stoichiometry with temperature for alumina supported palladium catalysts

T (K)	4.8%Pd/Al_2O_3		4.8%Pd/13%NaOH-Al_2O_3	
	N_{NO}/N_{Pd}	$-Q$ kJ (mol NO)$^{-1}$	N_{NO}/N_{Pd}	$-Q$ kJ (mol NO)$^{-1}$
220	0.10	116	0.12	140
250	0.10	115	0.12	138
280	0.10	115	0.12	140
300	0.10	120	0.12	141
320	0.11	105	0.16	130
370	0.11	176	0.32	174
420	0.10	209	1.0	220
470	0.12	230	1.2	245

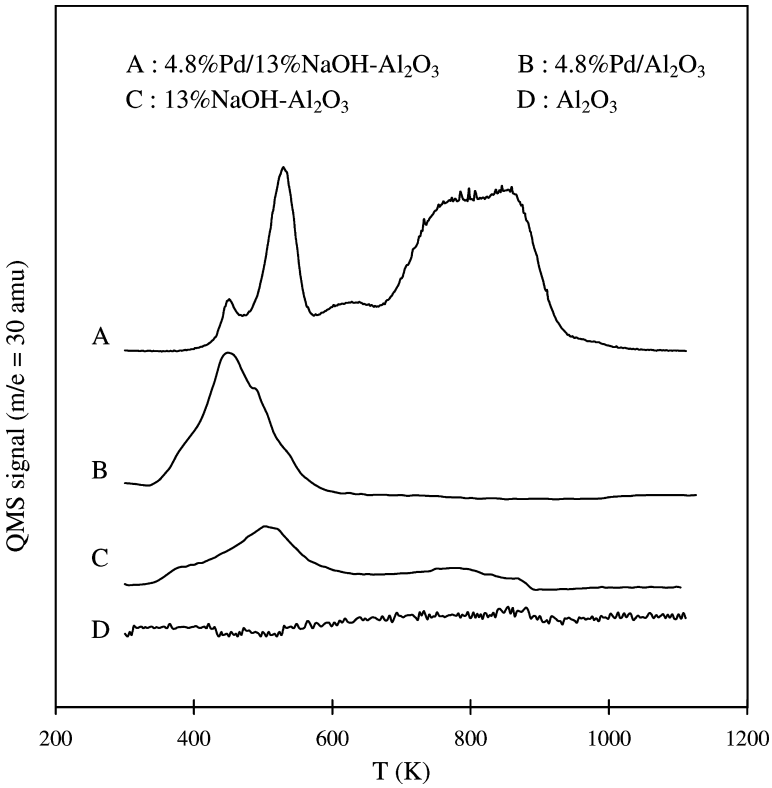

Fig. 2. Quadrupole mass measurement of the TPD–MS spectra for NO ($m/e = 30$ amu) adsorbed on various sample.

3.2. Temperature programmed desorption (TPD) of NO

All of the TPD data presented here are acquired in the same TG-DSC system following 300 K adsorption of NO on palladium surfaces. Fig. 2 shows the TPD–MS spectra of NO desorption ($m/e = 30$ amu) from four samples. The pure γ-Al_2O_3 support did not show significant NO desorption in the temperature range which could be attributed to the ordinarily inert for NO adsorbed. For un-promoted 4.8%Pd/Al_2O_3 catalyst and pure 13%NaOH-Al_2O_3 support, desorption of NO from these two samples occurred mainly at the region of ca. $350 \leq T \leq 580$ K and $350 \leq T \leq 600$ K, respectively. The attributions correspond to the weakly adsorbed NO. Yet for NaOH promoted 4.8%Pd/13%NaOH-Al_2O_3 catalyst, there exists three desorption peaks of NO in the NO-TPD spectrum which are located in the region of ca. $400 \leq T_1 \leq 440$ K, $450 \leq T_2 \leq 550$ K and $680 \leq T_3 \leq 950$ K, respectively. They may be attributed to desorption of NO from three sites of different adsorption strength, i.e., weakly adsorbed (desorbed at T_1 and T_2 regions) and strongly adsorbed (desorbed around T_3 regions) sites. In the thermal desorption measurements of NO on Pd(1 1 1), Conrad et al. [29] assigned three distinct states (weakly adsorbed: α and β

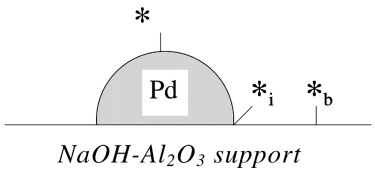

Fig. 3. Representation of NO adsorptive sites on Pd/NaOH-Al_2O_3 catalysts.

states; strongly adsorbed: γ state) corresponding to various binding energies. Accordingly, three types of NO adsorptive sites are assigned in Fig. 3 as Pd clusters (∗), basic sites ($*_b$) and Pd-NaOH interface sites ($*_i$). In comparison with above measurements, the adsorption of NO on the ∗ sites are relatively weak [integral $-\Delta H_{ad}$ around 114 kJ (mol NO)$^{-1}$] while the adsorption on the $*_b$ and $*_i$ sites are relatively strong [integral $-\Delta H_{ad}$ much higher than 140 kJ (mol NO)$^{-1}$].

Besides NO, other desorbates have been detected by mass-spectrometer. Fig. 4 presents TPD spectra obtained following 300 K adsorption of NO on an un-promoted 4.8%Pd/Al_2O_3

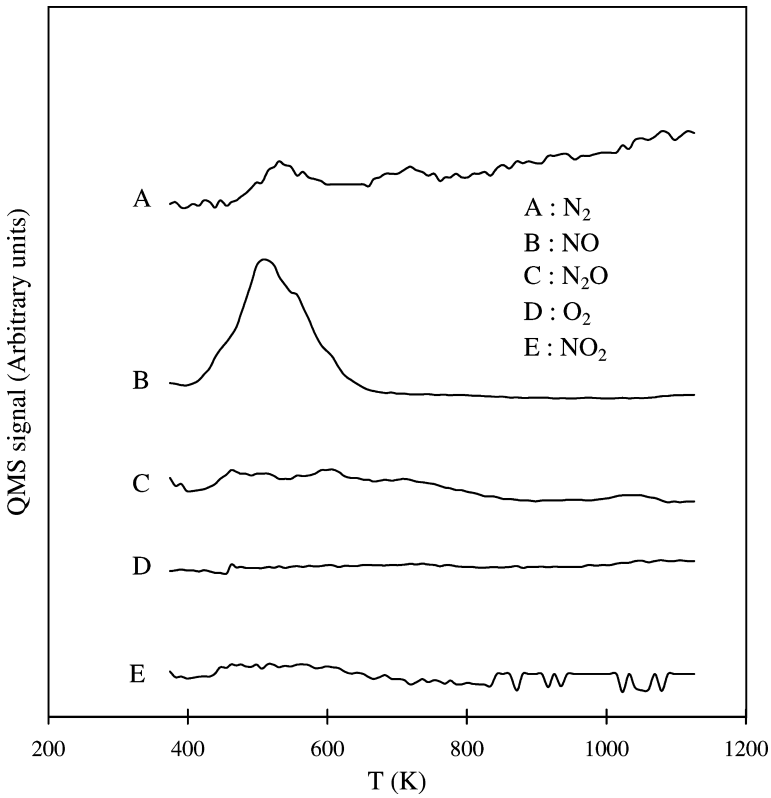

Fig. 4. TPD spectra for different desorbates from NO adsorbed on the 4.8%Pd/Al_2O_3 sample at 300 K.

sample. Upon heating, a large amount of NO adsorbed on the palladium surface is desorbed around $350 \leq T \leq 580$ K and a small amount of NO dissociation occurs on the palladium surface. The dissociated nitrogen atoms favor thermal desorption of N_2 species ($m/e = 28$ amu) at 550 K. While, the expected dioxygen desorption ($m/e = 32$ amu) at temperature higher than 1050 K is not observed in Fig. 4. This attributes to the dissociated oxygen atoms preferentially deposit on the palladium surface and penetrate into the sublayer region further oxidized the bulk palladium. In addition, no evidence for N_2O ($m/e = 44$ amu) or NO_2 ($m/e = 46$ amu) desorption observed. The results indicate that only minimal thermal decomposition of NO occurs on un-promoted 4.8%Pd/Al_2O_3 during heating. This conclusion is based on the small relative yields of NO dissociation products, N_2, observed during TPD, and is consistent with previous literature conclusions about the thermal behavior of NO on palladium single crystals [6,7,25,26,29–32].

Fig. 5 presents TPD spectra obtained following 300 K adsorption of NO on promoted 4.8%Pd/13%NaOH-Al_2O_3 sample. Besides minor NO (around 450 K) and N_2 (around 550 K) peaks, extra major peaks for desorption of N-containing species (NO_2, NO and N_2O) at the region of ca. $500 \leq T \leq 600$ K and a peak for O_2 desorption around $800 \leq T \leq$

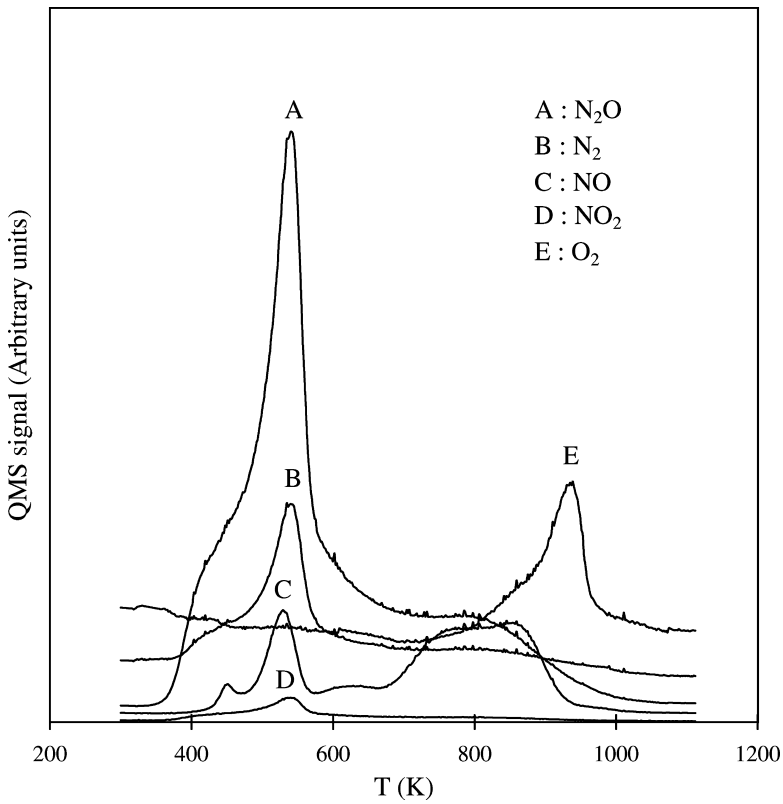

Fig. 5. TPD spectra for different desorbates from NO adsorbed on the 4.8%Pd/13%NaOH-Al_2O_3 sample at 300 K.

1000 K are found during heating. This indicates that the NO desorption and formation of these N-containing species may share the same rate-limiting step. Compared to un-promoted 4.8%Pd/Al_2O_3, the complicated results imply that the major difference is the presence of additional NO molecules adsorbed strongly on the $*_b$ and $*_i$ sites. The desorption of N-containing species should result from dissociation of weakly adsorbed NO on palladium surface into nitrogen and oxygen atoms around $400 \leq T \leq 600$ K. The dissociated nitrogen atoms may subsequently desorb into nitrogen molecules, or into N_2O upon combining with NO adsorbed strongly on $*_b$ and $*_i$ sites. The observed minor NO_2 desorbed in Fig. 5 may be formed through a surface reaction between the surface oxygen atoms that formed via the dissociation of weakly adsorbed NO and the strongly adsorbed NO on $*_b$ sites at lower temperature.

Nevertheless, the desorption of oxygen molecules at the region of ca. $800 \leq T \leq 1000$ K is quite surprising because the rate of oxygen desorption from surface of dispersed palladium crystallites was insignificant at this temperature ranges [33,34]. Observed lower temperature oxygen molecules desorption should be originated from the strongly adsorbed NO molecules and probably through a surface reaction between palladium surface bound oxygen atoms and the strongly adsorbed NO molecules on $*_i$ sites, i.e.

$$\text{NO-}*_i + \text{O-}* \rightarrow [\text{NO}_2\text{-}*_i] \rightarrow \text{NO} + \tfrac{1}{2}\text{O}_2 \tag{1}$$

In this reaction NO_2-$*_i$ represent a hypothetic intermediate which is probably found through diffusion of surface bound oxygen atoms to strongly adsorbed NO on $*_i$. Further, most of the intermediate simultaneously decomposed to NO and oxygen molecules at the region of ca. $800 \leq T \leq 1000$ K. These results are in agreement with the NO TPD spectra following NO_2 exposure on Pd (1 1 1) that NO_2 decomposes completely into NO and O upon heating above 600 K [6].

3.3. Mechanism for NO decomposition

According to the NO adsorption measurement and TPD results of this study, thermal decomposition of NO depends on the types of catalysts. Both un-promoted and promoted alumina supported palladium catalysts yield different mechanisms.

3.3.1. For Pd/Al_2O_3

The reactions involve in the adsorption and decomposition of NO on Pd/Al_2O_3 may be described as follows:

$$\text{NO} + * \Leftrightarrow \text{NO-}* \tag{2}$$

$$\text{NO-}* + * \rightarrow \text{N-}* + \text{O-}* \tag{3}$$

$$2\text{N-}* \rightarrow \text{N}_2 + 2* \tag{4}$$

$$2\text{O-}* \rightarrow \text{O}_2 + 2* \quad (\text{for } T \text{ higher than } 1050\text{ K}) \tag{5}$$

The most reasonable explanation for this proposition is that the presence of weakly adsorbed NO molecules acts to lower the activity of NO thermal decomposition.

3.3.2. For Pd/NaOH-Al_2O_3

The reactions involve in the adsorption and decomposition of NO on Pd/NaOH-Al_2O_3 may be described as follows:

$$\mathrm{NO} + * \Leftrightarrow \mathrm{NO}\text{-}* \quad (\text{including NO-}*_{\mathrm{b}} \text{ and NO-}*_{\mathrm{i}})$$

$$\mathrm{NO}\text{-}* + * \rightarrow \mathrm{N}\text{-}* + \mathrm{O}\text{-}*$$

$$2\mathrm{N}\text{-}* \rightarrow \mathrm{N_2} + 2*$$

$$2\mathrm{O}\text{-}* \rightarrow \mathrm{O_2} + 2* \quad (\text{for } T \text{ higher than } 1050\,\mathrm{K})$$

$$\mathrm{NO}\text{-}*_{\mathrm{b}} + \mathrm{N}\text{-}* \rightarrow \mathrm{N_2O} \tag{6}$$

$$\mathrm{NO}\text{-}*_{\mathrm{b}} + \mathrm{O}\text{-}* \rightarrow [\mathrm{NO_2}\text{-}*_{\mathrm{b}}] \rightarrow \mathrm{NO_2} \tag{7}$$

$$\mathrm{NO}\text{-}*_{\mathrm{i}} + \mathrm{O}\text{-}* \rightarrow [\mathrm{NO_2}\text{-}*_{\mathrm{i}}] \rightarrow \mathrm{NO} + \tfrac{1}{2}\mathrm{O_2} \quad (\text{for } T \text{ lower than } 950\,\mathrm{K})$$

The most reasonable explanation for this proposition is that the presence of strongly adsorbed NO molecules acts to promote the activity of NO thermal decomposition.

4. Conclusions

This report has presented a detailed comparison of NO adsorption and thermal behavior on both Pd/Al_2O_3 and Pd/NaOH-Al_2O_3 catalyst surfaces. The following results are found:

1. NO molecules are strongly adsorbed on promoted Pd/NaOH-Al_2O_3 and possess a higher enthalpy of adsorption [$\sim$140 kJ (mol NO)$^{-1}$] than un-promoted Pd/Al_2O_3 [$\sim$114 kJ (mol NO)$^{-1}$].
2. Upon heating, NO predominantly desorbs molecularly from Pd/Al_2O_3 around $350 \leq T \leq 580$ K. This indicates that only minimal thermal decomposition of NO occurs on un-promoted Pd/Al_2O_3 during heating.
3. Upon heating, relatively large amounts of N_2O and N_2, in addition to minor NO, desorb from Pd/NaOH-Al_2O_3 around $500 \leq T \leq 600$ K and large amounts of strongly adsorbed NO moleccules desorb around $680 \leq T \leq 950$ K. This indicates that the Na (an electron donor) shall enhance the chemisorption of NO (an electron acceptor) and increase its tendency to dissociation.

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