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Influence of palladium precursors on oxidation of alumina-supported palladium

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Abstract

The oxidation phenomena of alumina-supported palladium prepared from various precursors has been investigated by a simultaneous thermogravimetric analysis–differential scanning calorimetric (TGA–DSC) technique over a wide temperature range between 250 and 900 K. Three different temperature ranges were found in oxidation on Pd(C)/Al_2O_3: chemisorption of dioxygen at 250–300 K; penetration of adsorbed oxide ions into sublayers at temperature over 300 K; and formation of a stable bulk oxide at 800 K. However, four different temperature ranges were found on Pd(N)/Al_2O_3: chemisorption of dioxygen at 250–300 K and further formation of unstable Pd^sO_2 at 300–320 K; decomposition of Pd^sO_2 into Pd^s_xO at 320–420 K; penetration of adsorbed oxide ions into sublayers at temperature over 420 K; and formation of a stable bulk oxide at 800 K. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bulk; Surface; Oxidation; Thermally activated processes; Thermal properties

1. Introduction

Alumina-supported palladium is an important catalyst in catalytic oxidation of hydrocarbons [1–3] and nitric oxide (NO) pollutants catalytic conversion [4–6]. In these reactions, the mechanism involves the adsorption of oxygen on the surface of palladium and a reduction of the palladium oxide (by hydrocarbon or CO) back to palladium, i.e.,

$$Pd^s \Leftrightarrow Pd^sO_x \quad (1)$$

where x denotes an adsorption stoichiometry of oxygen on palladium atoms exposed on the surface (Pd^s) of dispersed palladium crystallites. The activity of the oxidation depends heavily on the nature of Pd^sO_x. Therefore, a detailed understanding of the interaction of palladium with dioxygen should be helpful towards improvements of the oxidation reactions.

In previous papers [7,8], we have explained the interaction of Pd/Al_2O_3 catalyst with dioxygen prepared from a H_2PdCl_4 precursor. The oxidation behavior was found to vary with the particle size of the palladium crystallites. In this work, I want to demonstrate and compare the distinctions of oxidation phenomena among the H_2PdCl_4 and $Pd(NO_3)_2$ precursors.

2. Experimental

2.1. Sample preparation

Pd(C)/Al_2O_3 or Pd(N)/Al_2O_3 samples of various palladium loadings were prepared by the incipient wetness method of impregnating hot H_2PdCl_4 or

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$Pd(NO_3)_2$ solution, respectively, into γ-Al_2O_3 (Merck, surface area $= 108\,m^2/g$). The slurries obtained were dried up overnight at 380 K and then calcined in air at 770 K for 4 h before storing as testing sample. The loading of palladium on these testing samples was determined by the atomic-emission technique using a Perkin-Elmer, Sciex Elan 5000 ICP-MS.

The dispersion (D, percentage of atoms exposed to surface) of palladium crystallites was measured by hydrogen chemisorption at 300 K under the assumption that $H/Pd^s = 1.1$ [9] at the monolayer chemisorption. Prior to chemisorption measurement, each sample was pretreated under a reducing condition by flowing hydrogen and evacuation at 570 K. Obtained dispersion of palladium on the samples is shown in Table 1.

Table 1
Dispersion and particle sizes for alumina-supported palladium measured at 300 K

Sample	Hydrogen chemisorption	
	D^a	d (nm)^b
4.80%Pd(N)	0.08	13.8
1.94%Pd(N)	0.09	12.2
0.95%Pd(N)	0.10	11.0
4.72%Pd(C)	0.21	5.2
2.04%Pd(C)	0.25	4.4
2.80%Pd(C)	0.30	3.7

[a] Dispersion of palladium crystallite.

[b] Average particle size.

2.2. Adsorption measurement

The amounts of dioxygen uptake and heats evolved on palladium samples were monitored over a temperature range between 250 and 900 K in a dual port calorimeter (Setaram TG-DSC 111) equipped with a sensitive balance (0.25 μg) and a calorimeter (10 μW). Before the dioxygen uptake, each testing sample was prereduced in flowing dihydrogen gas at 570 K for 1 h and a subsequent evacuation at 720 K for 1 h. The reduced sample was cooled in the Ar flow to a predetermined oxidizing temperature (T_{ox}) and then oxidized by a flow of 10 ml/min dioxygen introduced from the auxiliary inlet into the Ar flow. A detailed description of this system had been given in the previous report [7,8]. Pure γ-Al_2O_3 support was mounted in the reference port of the calorimeter as a blank to offset possible changes (Δm and ΔH) caused by the support.

3. Results and discussion

3.1. Dispersion measurements

Chemisorption is a basic technique to measure exposed percentages (or dispersion, D) of active metal in supported metallic catalysts [10,11]. In Table 1, the dispersion derived from hydrogen uptakes at 300 K and estimated palladium particles are given. The catalysts prepared from the H_2PdCl_4 lead to higher dispersion compared with those from $Pd(NO_3)_2$. This higher dispersion may be attributed to the presence of the interaction of chlorine in the H_2PdCl_4 precursor with alumina, which partially retains on the alumina support, after calcination treatment.

Based on XPS results, Stencel et al. [12] indicated two kinds of chlorine on supported platinum catalysts: one is associated with the metal and can be easily removed, while the other is associated with the support and is difficult to remove. So, the dispersion depending on the different types of supported species–support interaction on the palladium precursor is apparent.

3.2. Gravimetric measurements

The progressive oxidation was investigated by gravimetric and calorimetric measurements for different oxidation temperature under the same experimental conditions. Fig. 1 shows the temperature profiles of dioxygen uptake (in terms N_O/N_{Pd}) ratio observed after 2.5×10^3 s of oxidation on samples of 4.72%Pd(C)/Al_2O_3 (from H_2PdCl_4 precursor) and 4.80%Pd(N)/Al_2O_3 (from $Pd(NO_3)_2$ precursor). In this uptake study, a fresh sample was used in each data point. On raising the oxidation temperature from 250 to 900 K, each observed profile can easily discern three stages as previous reported [7] for Pd(C)/Al_2O_3 (some variations in the first and second stages for Pd(N)/Al_2O_3).

For Pd(C)/Al_2O_3 catalysts:

1. The N_O/N_{Pd} ratio remained at a constant plain value at $T < 300\,K(Pd_x^sO)$.

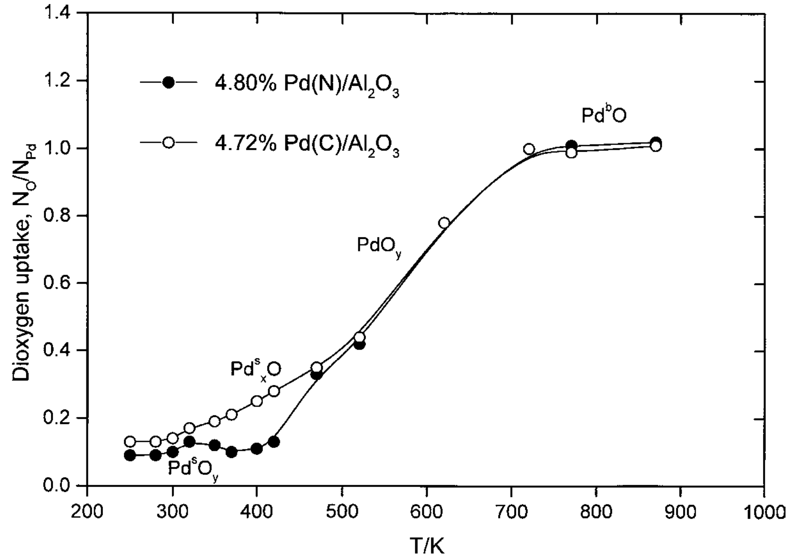

Fig. 1. Temperature profiles of dioxygen uptake on alumina-supported palladium metals: 4.80%Pd(N)/Al_2O_3 (●) and 4.72%Pd(C)/Al_2O_3 (○).

2. The ratio gradually increased from the plain value to a plateau value in the temperature range between 300 and 800 K (PdO$_y$).
3. The ratio remained at the plateau value in the temperature range between 800 and 900 K (Pd^{b}O).

The mechanism for Pd(C)/Al_2O_3 catalysts can, therefore, be the sequence of the following reactions:

$$Pd^s_xO \rightarrow PdO_y \rightarrow Pd^bO \qquad (2)$$

The three stages are assigned as chemisorption of dioxygen on the surface of palladium crystallites (Pd^s_xO), progressive penetration of adsorbed oxide ions into the sublayers (PdO_y), and formation of a stable bulk oxide structure (Pd^bO), respectively.

For Pd(N)/Al_2O_3 catalysts:

1. The N_O/N_{Pd} ratio slightly increased in the temperature range between 250 and 320 K (formation of unstable Pd^sO_2).
2. The ratio slightly decreased in the temperature range between 320 and 420 K (decomposition of Pd^sO_2 into Pd^s_xO).
3. The ratio gradually increased to a plateau value in the temperature range between 420 and 800 K (PdO_y).
4. The ratio remained at the plateau value in the temperature range between 800 and 900 K (Pd^bO).

The mechanism for Pd(N)/Al_2O_3 catalysts can, therefore, be the sequence of the following reactions:

$$Pd^sO_y \rightarrow Pd^sO_2 \rightarrow Pd^s_xO \rightarrow PdO_y \rightarrow Pd^bO \qquad (3)$$

The limitation to the surface adsorption at low temperatures implies not only the migration of adsorbed oxide ions into sublayers of palladium which has an energy barrier, but also that the thermal agitation at low temperatures was insufficient to overcome the barrier. On Comparison of Pd(C)/Al_2O_3 with Pd(N)/Al_2O_3 for Pd(C)/Al_2O_3 sample, the excessive oxidation for $T > 300$ K induced a formation of sublayer oxides. In the case of Pd(N)/Al_2O_3 sample, however, the oxidation preserved only a superficial character by formation of surface oxides—Pd^sO_2 and Pd^s_xO at temperature below 420 K. Clearly, the results indicate that Pd(N)/Al_2O_3 sample probably has a higher energy barrier than the Pd(C)/Al_2O_3 sample.

In previous literatures, Shaplygin et al. [13] suggested that palladium dioxide is unstable and begins to decompose in air at 340 K or when disturbed mechanically. Goncharenko et al. [14] also suggested that the dissociation of palladium dioxide occurred neighboring at 370 K. Similar result for Pd^sO_2 species obtained from Pd(N)/Al_2O_3 sample is thermodynamically unstable at temperature higher than 320 K, it decomposed to Pd^s_xO at higher temperature.

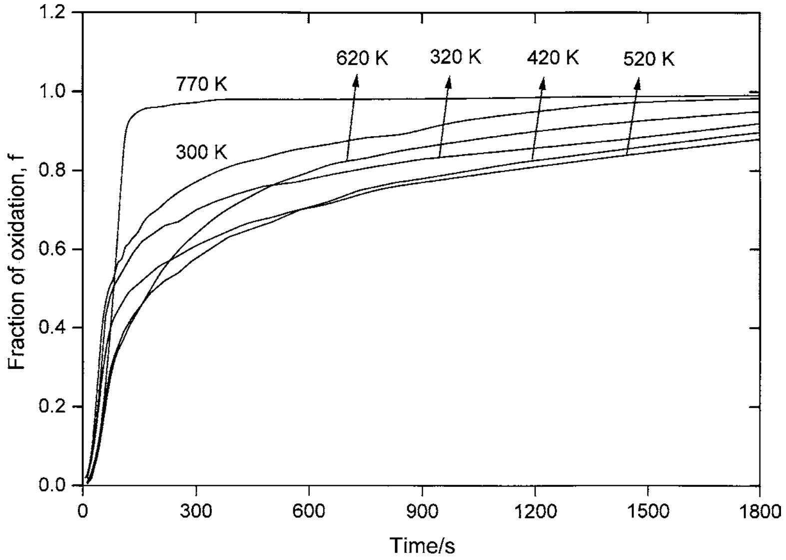

Fig. 2. Time profiles for the oxygen uptake fraction ($f = \Delta m_t/\Delta m$) of 4.72%Pd(C)/Al_2O_3 at various oxidation temperatures.

Figs. 2 and 3 present the time profile of the formation of oxygen uptake ($f = \Delta m_t/\Delta m$, where Δm_t and Δm denote the weight gained after an oxidation time t and after 2×10^3 s of oxidation, respectively) for 4.72%Pd(C)/Al_2O_3 and 4.80%Pd(N)/Al_2O_3 samples during various oxidation temperatures. An apparent decrease in the oxidation rate of the sample was found at 520 K for 4.80%Pd(N)/Al_2O_3 sample. The slowing down in the oxidation rate for the lower dispersed samples from nitrated precursor would imply that the penetration of oxide ions into sublayers of palladium has higher energy barrier than the higher dispersed samples from chlorated precursor. Lam and Boudart [15] and Palazov et al. [16] also found that the

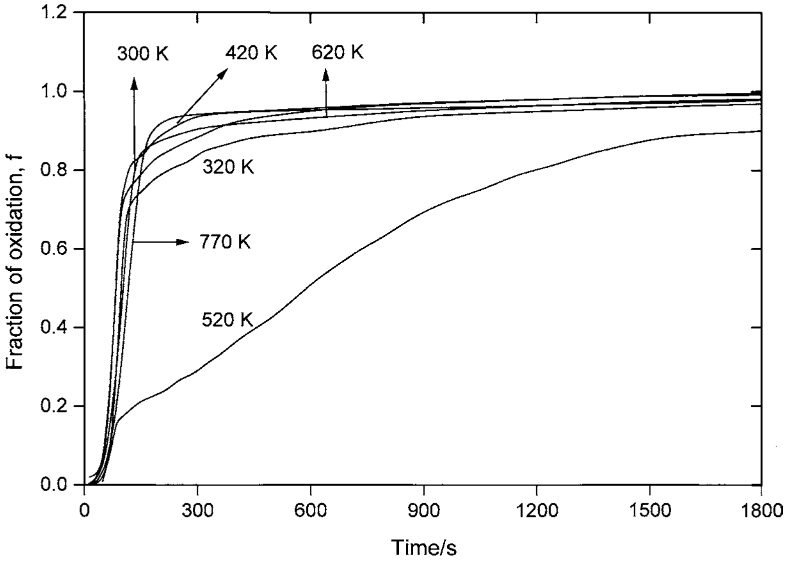

Fig. 3. Time profiles for the oxygen uptake fraction ($f = \Delta m_t/\Delta m$) of 4.80%Pd(N)/Al_2O_3 at various oxidation temperatures.

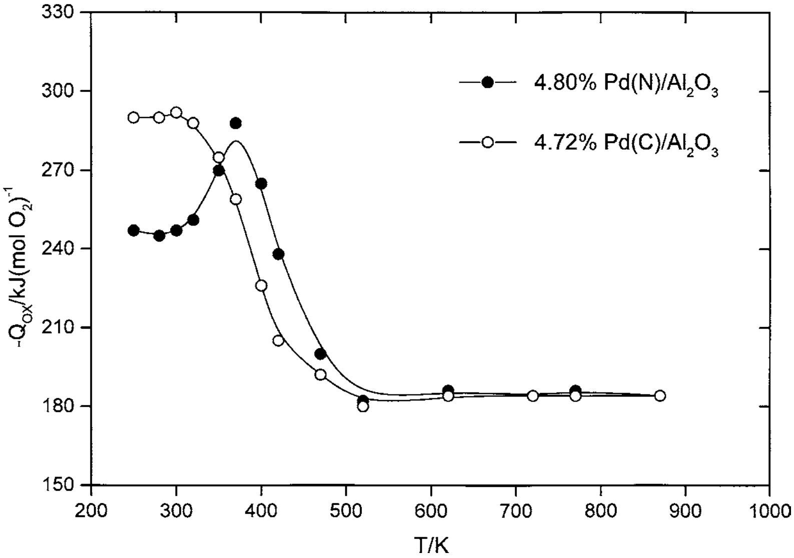

Fig. 4. Temperature profiles of heats of oxidation ($-Q_{ox}$) upon oxidation of alumina-supported palladium metals: 4.80%Pd(N)/Al_2O_3 (●) and 4.72%Pd(C)/Al_2O_3 (○).

penetration of oxide ions for the lower dispersion of palladium catalysts occurred at higher temperature (~550 K).

3.3. Calorimetric measurement

Fig. 4 compares the temperature profiles of heat evolution ($-Q_{ox}$) upon oxidation of the 4.72%Pd(C)/Al_2O_3 and the 4.80%Pd(N)/Al_2O_3 samples. Also, Table 2 shows the heat enthalpy ($-Q_{ox}$) and the N_O/N_{Pd} stoichiometry with temperature for both samples. The observed heat varies with the palladium precursor and the oxidation temperature. However, the three (or four) oxidation stages for Pd(C)/Al_2O_3 (or Pd(N)/Al_2O_3) described in the gravimetric measurement appeared again in this figure. For Pd(C)/Al_2O_3 sample, the heat of oxidation displayed a plateau value at the surface chemisorption ($T <$ 300 K); it gradually decreased on the penetration stage to a bottom value on the formation of a stable bulk oxide between 800 and 900 K. According to the definition of previous paper [7,8], the plateau value was the heat of oxygen adsorption ($-\Delta H_{ad}$), while the bottom value may be considered as the enthalpy of palladium oxide formation ($-\Delta H_f$). Apparently, the heat of adsorption is considerably higher than the heat of oxide formation and the extent of the adsorption is less than a monolayer; these features are indicative of true chemisorption as opposed to oxide formation. The higher the extents of oxidation, the lower the heats of oxidation evolved.

Contradistinction with Pd(C)/Al_2O_3 sample, the abruptly increased heat evolution over 320 K for

Table 2
Variations of heat enthalpy and N_O/N_{Pd} stoichiometry with temperature for alumina-supported palladium

T (K)	4.80%Pd(N)/Al_2O_3		4.72%Pd(C)/Al_2O_3	
	N_O/N_{Pd}	$-Q$ (kJ (mol O_2)$^{-1}$)	N_O/N_{Pd}	$-Q$ (kJ (mol O_2)$^{-1}$)
250	0.09	247	0.13	290
280	0.09	245	0.13	290
300	0.10	247	0.14	293
320	0.13	251	0.17	288
350	0.12	270	0.19	275
370	0.10	288	0.21	259
400	0.11	265	0.25	226
420	0.13	238	0.28	205
470	0.33	200	0.35	195
520	0.42	182	0.44	180
620	0.78	186	0.78	184
720	1.00	184	1.00	184
770	1.01	186	0.99	184
870	1.02	184	1.01	184

Table 3
Heats of dioxygen adsorption and heats of palladium oxide formation for various alumina-supported palladium

Sample	d (nm)	Oxygen adsorption		Formation of palladium oxide	
		N_O^{ad}/N_{Pd}[a]	$-\Delta H_{ad}$ (kJ (mol O_2)$^{-1}$)	N_O^{b}/N_{Pd}[b]	$-\Delta H_f$ (kJ (mol O_2)$^{-1}$)
4.80%Pd(N)	13.8	0.09	247	1.04	188
1.94%Pd(N)	12.2	0.07	263	1.02	180
0.95%Pd(N)	11.0	0.05	272	1.02	184
4.72%Pd(C)	5.2	0.14	293	1.05	184
2.04%Pd(C)	4.4	0.19	326	0.96	184
2.80%Pd(C)	3.7	0.21	330	1.04	188

[a] Uptake of oxygen atoms at 300 K.

[b] Uptake of oxygen atoms at 770 K.

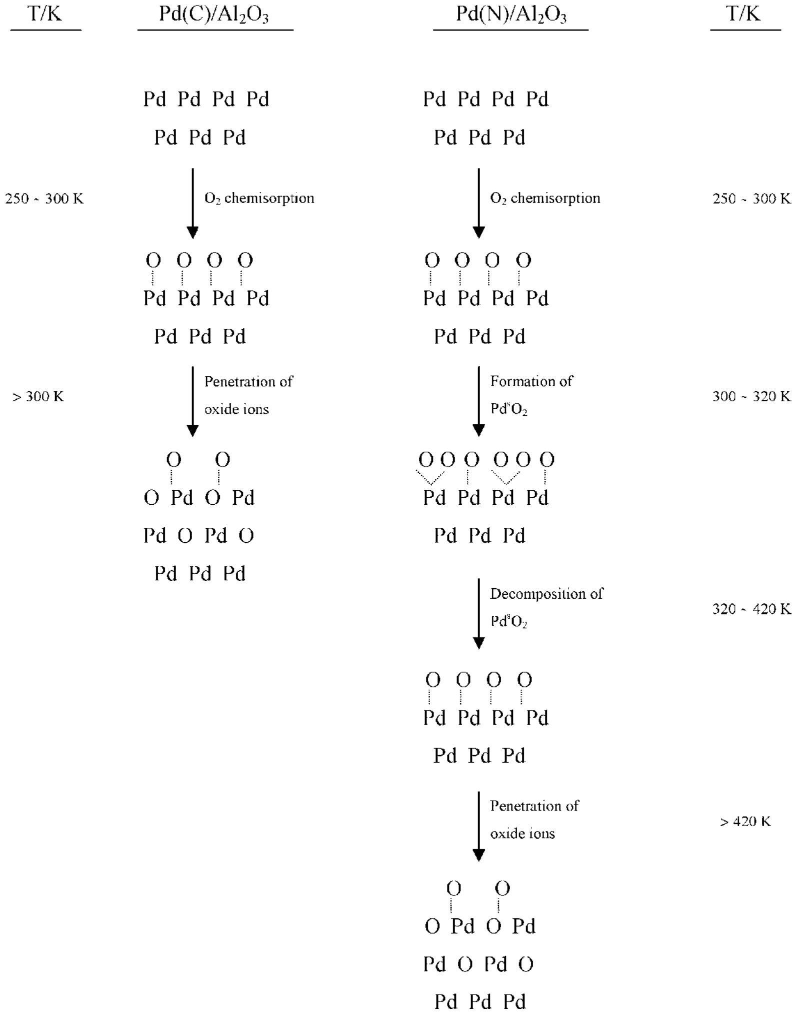

Fig. 5. Models proposed for temperature programmed oxidation from samples of Pd(N)/Al_2O_3 and Pd(C)/Al_2O_3.

$Pd(N)/Al_2O_3$ sample may be due to the strong bonding of Pd^s_xO formed by the following reactions:

$$Pd^s + \tfrac{1}{2}yO_2 \rightarrow Pd^sO_y \quad (4)$$

$$Pd^sO_y + O_2 \rightarrow Pd^sO_2 \quad (5)$$

$$Pd^sO_2 \rightarrow Pd^s + O_2 \quad (6)$$

$$Pd^sO_2 \rightarrow Pd^sO + \tfrac{1}{2}O_2 \quad (7)$$

$$xPd^s + \tfrac{1}{2}O_2 \rightarrow Pd^s_xO \quad (8)$$

In the temperature range between 250 and 320 K, the adsorption is accompanied at some stages by a change in oxidation number of the cations associated with the adsorbed layer via Eqs. (4) and (5) to form Pd^sO_y and Pd^sO_2 species. When the temperature raises over 320 K, the Pd^sO_2 becomes unstable and some reactions occur, i.e., desorption of oxygen from Pd^sO_2 species, formation of Pd^sO species through the slow decomposition of Pd^sO_2, and re-adsorption of oxygen on Pd^s through Eqs. (6)–(8). Since the strength of Pd^s_xO is higher than Pd^sO_y or Pd^sO_2 species, the obtained ΔH_{ad} arrives at the plateau value 370 K.

Table 3 lists dioxygen uptake on surface/bulk and heats of adsorption/formation for various alumina-supported palladium at 300/770 K. The crystallite size of supported palladium metal has a profound effect on the heat of adsorption. The evolved heat of adsorption increased to about $80\,\text{kJ}\,(\text{mol}\,O_2)^{-1}$ as the size of palladium crystallites was decreased from 13.8 to 3.7 nm. A decreasing of $-\Delta H_{ad}$ with the size of palladium crystallites has been previously noted by Zakumbaeva et al. [17], Chou and Vannice [18] and Ho et al. [7]. However, the heat evolved upon complete oxidation on palladium crystallites varies insignificantly with the diameter. The evolved heat of PdO species formation was $184 \pm 4\,\text{kJ}\,(\text{mol}\,O_2)^{-1}$ as the size of palladium crystallites decreased from 13.8 to 3.7 nm.

3.4. Mechanism of oxidation

According to the progressive oxidation with temperature measurement of this study, the low temperature oxidation for palladium crystallite depends on the kinds of catalyst precursor. Both catalysts prepared from H_2PdCl_4 and $Pd(NO_3)_2$ precursors give different mechanisms in the temperature range between 300 and 400 K. Fig. 5 displays a schematic diagram to describe the oxidation process on the $Pd(C)/Al_2O_3$ sample and the $Pd(N)/Al_2O_3$ sample. Within the same, a considerable increase in the uptake of oxygen occurs as the temperature is increased from 300 to 420 K for $Pd(C)/Al_2O_3$ and $Pd(N)/Al_2O_3$ sample, respectively. This growth can be ascribed to the mutual exchange of places of adsorbed oxide ions and the surface palladium atoms, i.e., the so-called place-exchange mechanism [19]. The penetration of oxide ions with deep chemisorption of oxygen as a result of the place-exchange mechanism, which is an activated process, increases as the temperature is increased. It seems possible that this step plays an important role in the complete bulk oxidation process. The results obtained show a great influence of an oxidation process with palladium precursors on the preparation of catalyst. This should be borne in mind when the preparation of palladium catalysts is being considered.

4. Conclusions

This report has presented a detailed comparison of oxidation process on both $Pd(C)/Al_2O_3$ and $Pd(N)/Al_2O_3$ samples. These experiments show the existence of Pd^sO_2 at lower temperature $(300\,\text{K} \leq T \leq 320\,\text{K})$ and decomposition of Pd^sO_2 at higher temperature $(320\,\text{K} \leq T \leq 420\,\text{K})$ on $Pd(N)/Al_2O_3$ sample. The penetration process starts at 300 K for $Pd(C)/Al_2O_3$ sample and at 420 K for $Pd(N)/Al_2O_3$ sample. Upon oxidation at 800 K, the formation of palladium oxide structure obtained.

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