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Composition of $Pd–La/\alpha\text{-}Al_2O_3$ catalysts

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The objective of this study is to investigate the structure of the $Pd–La/\alpha\text{-}Al_2O_3$ catalyst. X-ray diffraction (XRD) and temperature-programmed reduction (TPRd) were used as characterization techniques. Contrary to the assertions in the literature, XRD studies conducted on $La/\alpha\text{-}Al_2O_3$ composite oxides and $Pd–La/\alpha\text{-}Al_2O_3$ catalysts show that Pd catalyzes the solid state reaction between Al_2O_3 and Al_2O_3 to form $LaAlO_3$. TPRd studies conducted on $Pd/\alpha\text{-}Al_2O_3$, Pd/La_2O_3, $Pd/LaAlO_3$, and $Pd–La/\alpha\text{-}Al_2O_3$ catalysts suggest that Pd in the $Pd–La/\alpha\text{-}Al_2O_3$ catalyst interacts more strongly with $LaAlO_3$ than with $\alpha\text{-}Al_2O_3$. Reaction studies were conducted to investigate the activity of $Pd/\alpha\text{-}Al_2O_3$, Pd/La_2O_3, $Pd/LaAlO_3$, and $Pd–La/\alpha\text{-}Al_2O_3$ catalysts for nitric oxide (NO) reduction. These studies show that $Pd/LaAlO_3$ catalysts are most active for NO removal at stoichiometric and under net reducing conditions.

Keywords: Palladium; lanthanum; lanthanum oxide; lanthanum aluminum oxide; α-alumina; X-ray diffraction (XRD); temperature-programmed reduction (TPRd); nitric oxide

1. Introduction

Since palladium (Pd) is more readily available and cheaper compared to rhodium (Rh), the current emphasis in automotive catalysis is to develop three-way catalysts (TWCs) with Pd as the major component. However, the Pd catalyst has poor NO reduction capability and a narrower operating window compared to a Rh catalyst. Base metal oxide [1,2] and rare earth oxide [3,4] modified Pd catalysts have been investigated in an attempt to improve the NO conversion of Pd catalysts. It has been observed that the $Pd–La/\alpha\text{-}Al_2O_3$ catalyst shows high activity for NO removal from automotive exhaust streams under stoichiometric as well as reducing conditions [3,4].

The study of $Pd–La/\alpha\text{-}Al_2O_3$ catalysts has been of interest. It has been proposed that $\alpha\text{-}Al_2O_3$ does not undergo solid state reactions with La_2O_3 under typical TWC operating conditions [5]. It has been shown that the higher NO

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reduction activity of the Pd–La/α-Al_2O_3 catalyst is due to its higher activity for the water–gas shift reaction [6]. The durability of the Pd–La/α-Al_2O_3 catalyst for automotive exhaust treatment has also been investigated [7]. Characterization studies using temperature-programmed reduction (TPRd), X-ray photoelectron spectroscopy (XPS), and propylene chemisorption show that the addition of lanthana to a Pd/α-Al_2O_3 catalyst renders the reduction of supported PdO more difficult and suppresses hydrocarbon (HC) chemisorption, thereby moderating HC poisoning [8].

The investigation of Pd–La interactions in Pd/La_2O_3 catalysts has also been an area of interest. It has been observed by XPS that the binding energy of Pd supported on La_2O_3 is lower than that of Pd metal foil by as much as 0.8 eV [9]. These investigators concluded that La chemically modifies Pd due to metal–support interactions. Subsequently, it has been speculated based on the excess H_2 and O_2 consumptions observed during temperature-programmed reduction (TPRd) and temperature-programmed oxidation (TPO) experiments, that a fraction of the Pd surface in the Pd/La_2O_3 catalyst is covered by the partially reduced LaO_x entity [10].

The objective of the present investigation is to study the morphology of the Pd–La/α-Al_2O_3 catalyst. X-ray diffraction (XRD) and TPRd were used as characterization techniques. XRD studies were conducted to investigate the morphological changes occurring in the La/α-Al_2O_3 composite oxide in the presence of Pd. These investigations show that Pd catalyzes the solid state reaction between La_2O_3 and Al_2O_3 to form $LaAlO_3$. TPRd studies were used to assess the distribution of Pd in the Pd–La/α-Al_2O_3 catalyst. These studies suggest that Pd strongly interacts with $LaAlO_3$. The NO reduction activity of Pd/$LaAlO_3$, Pd/La_2O_3, Pd/α-Al_2O_3, and Pd–La/α-Al_2O_3 catalysts was compared. These investigations show that the Pd/$LaAlO_3$ catalyst has the highest NO reduction activity under stoichiometric and reducing conditions.

2. Experimental

Materials. Lanthana (Kerr McCee Corp.), α-alumina (Aldrich Chemicals), and γ-alumina (Degussa, Al_2O_3-C) with surface areas of 8.00, 10.07, and 100.0 m^2/g, respectively, were used as supports during this study.

Preparation of lanthanum aluminum oxide. Lanthanum nitrate (Aldrich Chemicals) and aluminum nitrate (Alfa Chemicals) were dissolved in deionized water and heated to form a viscous mass which crystallized on cooling. The solid was ground and calcined at 1000°C for 48 h. Since the amount of lanthanum nitrate used was slightly in excess of stoichiometry, lanthanum aluminum oxide and lanthanum oxide were present in the product obtained after calcination. The XRD analysis of the material did not show patterns corresponding to the presence of alumina. The difference in the solubility of La_2O_3 and $LaAlO_3$ in

Table 1
XRF analyses for Pd and La loadings

Catalyst	Pd weight loading (%)	La weight loading (%)
Pd/α-Al_2O_3	1.21	–
Pd/La_2O_3	1.20	–
Pd/$LaAlO_3$	1.24	–
Pd–La/α-Al_2O_3	1.23	4.68

dilute nitric acid was utilized to purify the $LaAlO_3$–La_2O_3 mixture. The XRD analysis of the solid obtained after the nitric acid treatment did not show the presence of La_2O_3. The BET surface area was measured by nitrogen adsorption [11]. Here, the area of a nitrogen molecule was assumed to be 16.2 Å^2. $LaAlO_3$ had a BET surface area of 2.43 m^2/g.

Preparation of composite oxide. Lanthanum nitrate solutions of desired concentrations were contacted with γ-Al_2O_3 and α-Al_2O_3. The precursors were dried at 120°C for 1 h and later calcined to form the 4.68% La/α-Al_2O_3 (calcined at 600°C for 6 h), 9.5% La/α-Al_2O_3 (calcined at 1200°C for 6 h), and 9.5% La/γ-Al_2O_3 (calcined at 1200°C for 6 h) composite oxides.

Preparation of catalysts. A palladium nitrate solution of desired concentration was contacted with α-Al_2O_3, La_2O_3, $LaAlO_3$, and 4.68% La/α-Al_2O_3 composite oxide. The precursors were dried at 120°C (for 1 h) and later calcined at 600°C (for 6 h). The product obtained after calcination is called catalyst. The catalysts had a nominal Pd loading of 1.2%; the exact values, as determined by X-ray fluorescence (XRF) spectroscopy, are shown in table 1.

X-ray fluorescence spectroscopy. The Pd and La weight loadings in the catalyst samples were determined by XRF spectroscopy. A model SRS 303 Siemens X-ray spectrometer equipped with a chromium X-ray tube operating at 60 kV and 50 mA was used for the analysis. The Pd analysis consisted of measuring the intensity of the Pd Kα1 X-ray line with a LiF(220) diffracting crystal and scintillator detector, whereas, the La Lα1 X-ray line was measured using a LiF(200) diffracting crystal with a P-10 gas (90% argon, 10% methane) flow detector. Measured X-ray intensities were normalized for possible instrumental variations and then corrected for detector dead-time. Average background measurements for each X-ray line were determined and subtracted from peak intensities. Single element calibration standards for Pd and La were used to determine the approximate Pd and La weight loadings first. The approximate weight loading was subsequently corrected for inter-element effects by using the Artz influence coefficient correction method [12].

X-ray diffraction. X-ray diffraction analyses were conducted using a vertical powder diffractometer, equipped with a diffracted beam monochromator, and Cu Kα radiation ($\lambda = 1.542$ Å).

Temperature-programmed reduction. The TPRd experiments were conducted using an Altamira AMI-1 apparatus. Typically 200 mg of sample was used during the experiment. The sample was first dehydrated in a stream of flowing Ar at 150°C and later cooled to −50°C using liquid nitrogen. The 8.85% H_2/Ar stream was allowed to flow over the sample and the temperature of the sample was linearly raised from −50°C to 650°C at 20°C/min. The hydrogen consumption was monitored as a function of temperature using a thermal conductivity detector.

Flow reactor studies. Flow reactor studies were conducted using an integral reactor [13]. A catalyst sample of 0.2 g was used in the experiments and the reaction temperature was 550°C. The NO conversions of the catalysts were investigated using a simulated automobile exhaust gas mixture that contained 1000 ppm NO, 20 ppm SO_2, 20000 ppm water vapor, 15000 ppm CO, 167 ppm C_3H_8, 333 ppm C_3H_6, and 5000 ppm H_2. The oxygen concentration of the gas stream at the inlet of the reactor was varied between 20000 ppm and 6400 ppm to vary the redox ratio (R) between 0.6 and 1.8. (The redox ratio is the ratio of the reducing components to the oxidizing components in the gas mixture.) Nitrogen was used as the carrier gas and the total gas flow rate was 3000 (std) cm^3/min. The above conditions correspond to a space velocity of 900000 cm^3/(hg of catalyst).

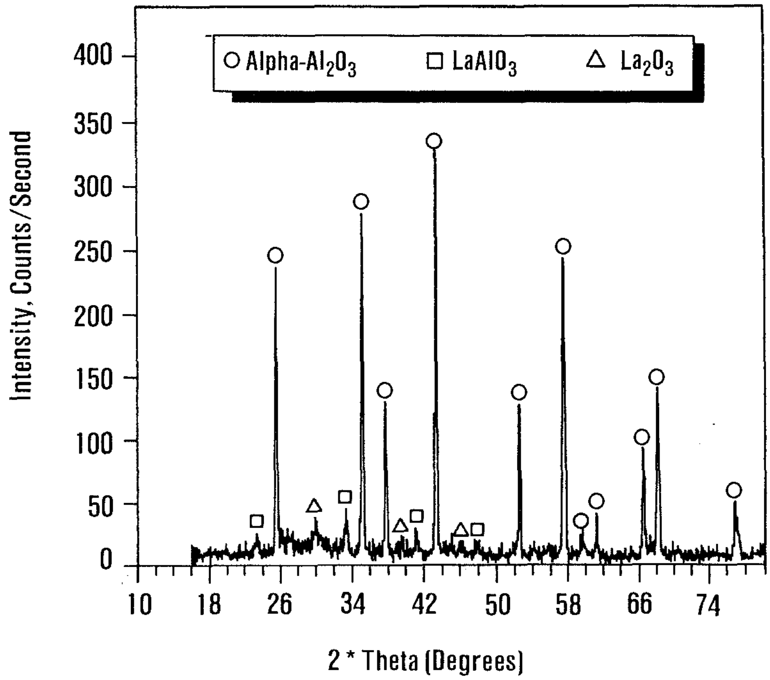

Fig. 1. XRD pattern of 4.7% La/α-Al_2O_3 composite oxide.

3. Results

The XRD pattern of the 4.68% La/α-Al_2O_3 composite oxide is shown in fig. 1. The composite oxide contains $LaAlO_3$, crystalline La_2O_3, and α-Al_2O_3. Approximately 80% of La appears to be present as La_2O_3, the remaining 20% is present as $LaAlO_3$. This shows that $LaAlO_3$ formation occurs when an α-Al_2O_3 supported lanthanum nitrate precursor is calcined at 600°C. The XRD pattern for the Pd–La/α-Al_2O_3 catalyst is shown in fig. 2. Analysis of the diffraction pattern indicates that this catalyst contains $LaAlO_3$ and α-Al_2O_3. The short range order peak (deviation from the baseline resulting in a hump) observed between 26° and 34° suggests that relatively small amounts of La_2O_3 may be present in an amorphous form. TPRd studies were conducted to assess the distribution of Pd in Pd–La/α-Al_2O_3 catalysts. The TPRd trace for Pd/α-Al_2O_3, Pd/La_2O_3, Pd/$LaAlO_3$, and Pd–La/α-Al_2O_3 catalysts are shown in figs. 3a–3d, respectively. The peak temperatures, the H/M ratio, and the percentage of total H_2 consumed at temperatures less than 300°C are reported in table 2. The NO oxide reduction activity is shown in the form of a plot of NO conversion versus R (fig. 4). Here $R > 1$ refers to net reducing conditions and $R < 1$ refers to net oxidizing conditions. The feed gas is stoichiometric when

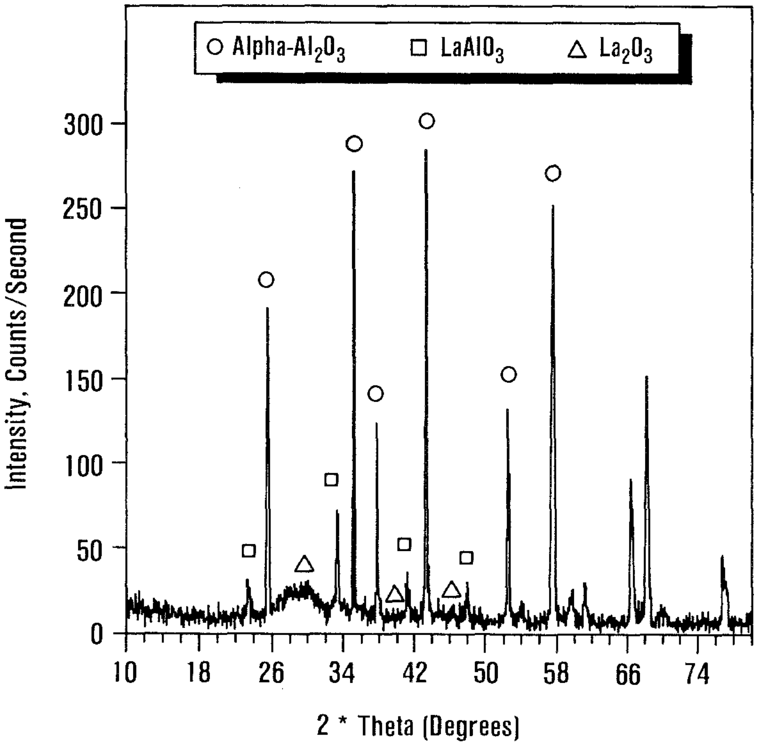

Fig. 2. XRD pattern of Pd–La/α-Al_2O_3 catalyst.

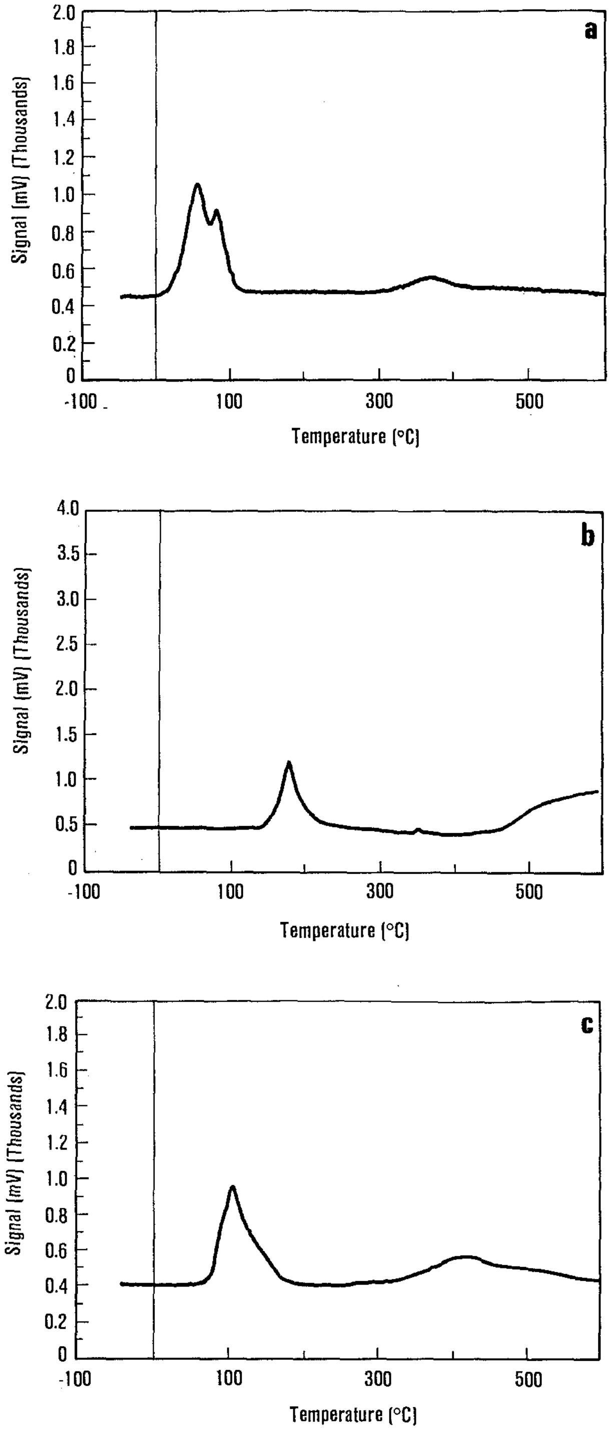

Fig. 3. TPRd trace for (a) Pd/α-Al_2O_3, (b) Pd/La_2O_3, (c) Pd/$LaAlO_3$, (d) Pd–La/α-Al_2O_3.

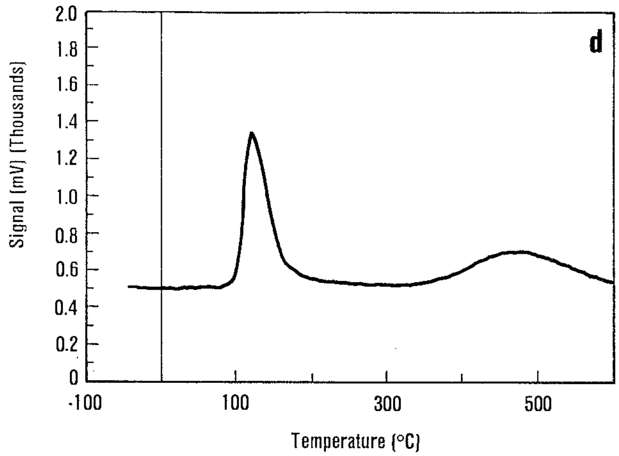

Fig. 3 (continued).

$R = 1$. It is observed that the Pd/$LaAlO_3$ catalyst shows the highest NO conversion under stoichiometric as well as reducing conditions.

4. Discussion

4.1. X-RAY DIFFRACTION

Comparison of figs. 1 and 2 shows that there is an increase in the intensity of the $LaAlO_3$ peaks when the 4.68% La/α-Al_2O_3 oxide is calcined after the addition of Pd. (Recall that these samples were calcined at the same tempera-

Table 2
Peak temperature, H/M ratio and percentage of total H_2 consumed at temperatures less than 300°C during TPRd

Catalyst	TPRd results		
	peak temperature (°C)	H/M	percentage of total H_2 consumed at temperatures < 300°C
Pd/α-Al_2O_3	55, 82, 370	2.20	84.0
Pd/La_2O_3	177 [a]	2.68 [b]	[c]
Pd/$LaAlO_3$	103, 418	4.03	53.8
Pd-La/α-Al_2O_3	119, 472	4.82	49.6

[a] Reduction at $T > 500$°C.

[b] H/M calculated based on the hydrogen consumption observed at temperatures less than 300°C. The hydrogen consumption occurring at temperatures greater than 500°C was not included.

[c] Cannot be determined quantitatively.

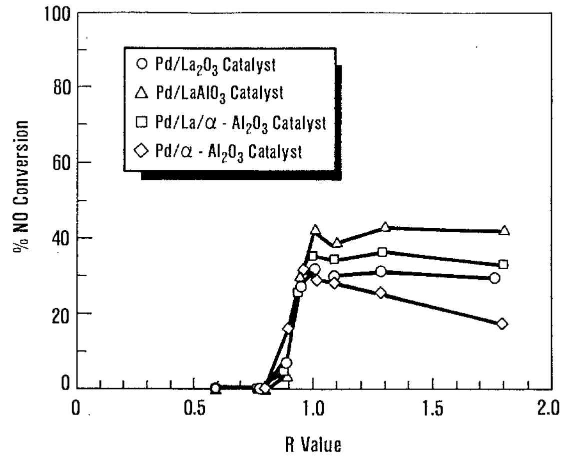

Fig. 4. NO conversion for Pd/α-Al_2O_3, Pd/La_2O_3, Pd/$LaAlO_3$ and Pd-La/α-Al_2O_3. The following experimental conditions were used: The feed gas contained 167 ppm C_3H_8, 333 ppm C_3H_6, 15000 ppm CO, 5000 ppm H_2, 1000 ppm NO, 20 ppm SO_2, and 20000 ppm H_2O. The O_2 concentration was varied and the catalyst temperature was held constant at 550°C.

ture, i.e. 600°C.) As shown in table 3, the relative intensity of the strongest line for $LaAlO_3$ increases. The peak characteristic of La_2O_3 at 30.0° (fig. 1) can be barely identified in fig. 2. This indicates that a significant fraction of the crystalline La_2O_3 originally present was transformed to $LaAlO_3$ in the presence of Pd. A relatively small fraction of the La appears to be present as amorphous La_2O_3 as seen from the short range order peak observed between 26° and 34° in fig. 2.

Lanthana is known to dissolve in acidic $Pd(NO_3)_2$ impregnation solutions [14]. The loss of La_2O_3 and the formation of $LaAlO_3$ could occur during the impregnation of Pd. Alternatively, Pd could catalyze the chemical reaction between La_2O_3 and α-Al_2O_3 to form $LaAlO_3$. X-ray diffraction studies were conducted to identify the role of Pd in increasing the $LaAlO_3$ content of the Pd-La/α-Al_2O_3 catalyst. Pd was impregnated on the 4.68% La/α-Al_2O_3 composite from a $Pd(NO_3)_2$ solution by incipient wetness and the resulting material was dried at 120°C for 1 h. The XRD pattern of this entity was similar to that of

Table 3
Relative $LaAlO_3$ peak intensities in 4.68% La/α-Al_2O_3 and Pd-La/α-Al_2O_3 catalysts

Materials	Intensity of strongest line (counts/s)		Ratio of intensities [c]
	α-Al_2O_3 [a]	$LaAlO_3$ [b]	
4.68% La/α-Al_2O_3	329	44	0.13
Pd-La/α-Al_2O_3	285	72	0.25

[a] Intensity of line at 43.4°.
[b] Intensity of line at 33.4°.
[c] Ratio of the intensities of the strongest lines for $LaAlO_3$ and α-Al_2O_3.

the 4.68% La/α-Al_2O_3 composite oxide. This suggests that $LaAlO_3$ formation does not occur during the aqueous phase impregnation of Pd. The Pd impregnated La/α-Al_2O_3 was calcined at 400°C for 6 h. XRD analysis of this material was also similar to that of La/α-Al_2O_3. This observation suggests that Pd may catalyze the solid state reaction between La_2O_3 and α-Al_2O_3 in the 400 to 600°C temperature range.

Investigators studying Pd–La/α-Al_2O_3 have proposed that α-Al_2O_3 does not undergo solid state reactions with La_2O_3 to form $LaAlO_3$ in such a catalyst [5,6]. These investigators conducted their studies on a cordierite supported Pd–La/α-Al_2O_3 catalyst whereas Pd–La/α-Al_2O_3 powder samples were used in the present study. It is, however, known that the addition of La improves the thermal stability of the γ-alumina [15]. It has been proposed that the addition of La to γ-Al_2O_3 lowers the sintering rate of γ-Al_2O_3 due to the formation of a lanthanum aluminum oxide ($LaAlO_3$) surface layer [16,17]. One to one comparisons between α-Al_2O_3 and γ-Al_2O_3 are difficult because of the differences in their crystal structure. The thermodynamic stability of La_2O_3 and $LaAlO_3$ in α-Al_2O_3 and γ-Al_2O_3 was compared.

The 9.5% La/α-Al_2O_3 and 9.5% La/γ-Al_2O_3 composite oxides, calcined at 1200°C (for 6 h), were investigated by XRD. These studies showed the presence of $LaAlO_3$ in the former and $La_2O_3 \cdot 11Al_2O_3$ and $LaAlO_3$ in the latter. La_2O_3 was not observed in either case. This suggests that La is more stable as $LaAlO_3$ rather than as La_2O_3 in La/α-Al_2O_3 and La/γ-Al_2O_3 composite oxides. These considerations support our observation that $LaAlO_3$ is formed in Pd–La/α-Al_2O_3 catalysts.

4.2. TEMPERATURE-PROGRAMMED REDUCTION

The TPRd trace of Pd/α-Al_2O_3 shows peaks at 55, 82 and 370°C (fig. 3a). It is known that the TPRd of supported PdO is complicated by factors such as Pd–H formation and support reduction [18–20]. It has been proposed that supported PdO exists in two phases, crystalline PdO and 2D surface PdO. The reduction of supported crystalline PdO is complete before 160°C [19,20]. The two-dimensional surface PdO reduces in the 300–500°C range. In the case of γ-Al_2O_3 supported Pd, it is known that a negative peak corresponding to the decomposition of bulk β-$Pd{-}H_{0.6}$ is observed at 88°C [19].

It has been proposed that the hydride formation precedes hydride decomposition [21]. These investigators propose that the following processes result in H_2 consumption during TPRd of a Pd/γ-Al_2O_3 catalyst:

$$Pd_{(s)}O + H_2 \rightarrow Pd_{(s)} + H_2O, \tag{1}$$

$$Pd_{(b)}O + H_2 \rightarrow Pd_{(b)} + H_2O, \tag{2}$$

$$Pd_{(s)} + (1/2)H_2 \rightarrow Pd_{(s)}H, \tag{3}$$

$$Pd_{(b)} + (n/2)H_2 \rightarrow Pd_{(b)}H_n. \tag{4}$$

Here subscripts s and b refer to surface and bulk species respectively, and n is a number that depends on the H_2 partial pressure and temperature. They also propose that the negative peaks or hydrogen evolution results from

$$Pd_{(s)}H \rightarrow Pd_{(s)} + (1/2)H_2, \tag{5}$$

$$Pd_{(b)}H_n \rightarrow Pd_{(b)} + (n/2)H_2. \tag{6}$$

Based on the above considerations it is speculated that the peaks observed at 55 and 82°C result from the superposition of hydride decomposition on the reduction of crystalline or bulk PdO. The reduction peak observed at 370°C is attributed to the reduction of surface PdO. The H/M ratio observed (table 2) is within experimental error of that expected based on the reduction stoichiometry of PdO (stoichiometric H/M value is 2.0).

It is seen that $Pd/LaAlO_3$, Pd/La_2O_3, and Pd–La/α-Al_2O_3 reduce at a higher temperature than the Pd/α-Al_2O_3 catalyst. This is in agreement with the observation reported that the addition of La retards the reducibility of a Pd/α-Al_2O_3 catalyst [8]. It is also observed (fig. 3b) that significant amounts of H_2 are consumed at temperatures higher than 500°C during the reduction of Pd/La_2O_3. The H/M values (table 2) for the La containing catalysts indicate that the observed H_2 consumption is in excess of that required for the stoichiometric reduction of PdO. These observations are similar to those reported on La modified Pd/SiO_2 catalysts [9]. It has been suggested that hydrogen adsorbs on the surface of Pd and diffuses to the Pd–La_2O_3 interface leading to species with stoichiometries such as $LaPd_xO$ [9].

It is interesting to note that the La containing catalysts do not show a hydrogen evolution peak corresponding to the decomposition of palladium hydride. XPS studies have shown that La modifies the chemical behavior of Pd due to metal–support interactions [9]. This suggests that the hydride formation process is suppressed by metal–support interactions. This observation is consistent with that reported in the literature [22]. These investigators conclude based on the temperature resolved sorption studies of TiO_2, Al_2O_3, SiO_2, and C supported Pd catalysts that the SMSI phenomenon suppresses the absorption of H_2 in bulk Pd.

The TPRd trace of Pd–La/α-Al_2O_3 was compared with that of $Pd/LaAlO_3$, Pd/La_2O_3, and Pd/α-Al_2O_3. The comparisons were made using three criteria, peak temperature, H/M ratio, and percentage of total H_2 consumed at temperatures less than 300°C (table 2). During the TPRd of Pd/La_2O_3, the maximum in reduction rate occurs at 177°C. The TPRd trace for Pd–La/α-Al_2O_3 does not show reduction at 177°C. Likewise, Pd/La_2O_3 shows H_2 consumption at temperatures greater than 500°C; no reduction is observed at temperatures greater than 500°C during the TPRd of Pd–La/α-Al_2O_3. It is seen that the TPRd profile of the Pd–La/α-Al_2O_3 catalyst resembles that of the Pd/$LaAlO_3$ catalyst. Recall, that XRD studies showed that La in the Pd–La/α-Al_2O_3 catalyst is predominantly present as $LaAlO_3$. These considerations suggest that Pd in the Pd–La/α-Al_2O_3 catalyst interacts more strongly with $LaAlO_3$ than with α-Al_2O_3.

4.3. NO REDUCTION ACTIVITY

Studies reported in the literature have shown that the NO reduction activity of a Pd–La/α-Al_2O_3 catalyst is higher than that of a Pd/α-Al_2O_3 catalyst when the feed gas is stoichiometric or net reducing in nature [5–8]. Our interest in this study is to compare the NO reduction activity of Pd–La/α-Al_2O_3 with that of Pd/La_2O_3, Pd/$LaAlO_3$, and Pd/α-Al_2O_3 catalysts. It is interesting to note (fig. 4) that the NO reduction activity decreases in the order Pd/$LaAlO_3$ > Pd–La/α-Al_2O_3 > Pd/La_2O_3 > Pd/α-Al_2O_3. The CO and hydrocarbon oxidation activity observed around the stoichiometric point are highest in the case of the Pd–La/α-Al_2O_3 catalyst. The conversions observed in the present study are lower than those reported in the literature [4]. These differences in the configuration of the catalysts (monolith versus powder samples), the La and Pd loadings, and the space velocity may account for the differences in activities.

5. Conclusions

It has been shown that a fraction of La_2O_3 reacts with the α-Al_2O_3 to form $LaAlO_3$ when an α-Al_2O_3 supported lanthanum nitrate precursor is calcined at 600°C. When the La/α-Al_2O_3 composite oxide is used as support for a Pd catalyst, Pd catalyzes the reaction between La_2O_3 and α-Al_2O_3 resulting in an increase in the amount of $LaAlO_3$ formed. The TPRd characterization studies suggest that Pd in the Pd–La/α-Al_2O_3 catalyst interacts more strongly with $LaAlO_3$ rather than with α-Al_2O_3. Reaction studies show that the NO reduction activity under stoichiometric and reducing conditions decreases in the order: Pd/$LaAlO_3$ > Pd–La/α-Al_2O_3 > Pd/La_2O_3 > Pd/α-Al_2O_3.

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