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Characterization and temperature-programmed studies over Pd/TiO_2 catalysts for NO reduction with methane

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Abstract

Characterization and temperature-programmed studies were performed over Pd/titania catalysts to examine their activity in the reduction of NO with methane. The catalyst was prepared using a wet impregnation technique and Pd-acetate was used as a precursor for palladium. Techniques such as BET surface area measurements, X-ray diffraction, laser Raman spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy were used for the characterization of the catalyst before and after the reaction. Temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) were also used to probe the surface to understand its adsorption/desorption characteristics and reducing capabilities. The results obtained from these studies together with the reaction investigations have given some important insight into the functionality of this catalyst. © 1998 Elsevier Science B.V.

Keywords: No reduction; Methane; XPS; TPR; TPD; Palladium; Titania

1. Introduction

NO reduction with hydrocarbons, specially lower hydrocarbons, has become an increasingly important [1–6] area of research. NO_x emissions from automobile as well as stationary sources have been responsible for deterioration of the environment in many parts of the world. In the past, we have investigated the use of ammonia as a reducing agent for limiting NO emissions from stationary combustion sources such as internal combustion engines and boilers [7–10]. Despite the fact that ammonia is a selective reducing agent, in practical applications it has several disadvantages such as corrosion due to ammonium salts, transportation, and storage issues. These concerns have rendered hydrocarbons as economically favorable reducing agents for NO_x reduction.

Palladium-based catalysts are well-known for their ability to activate hydrocarbons, especially methane, in partial and complete oxidation reactions. Palladium is also an important constituent of three-way catalysts for controlling automobile emissions. Stricter hydrocarbon emission regulations imposed in several parts of North America and Europe have prompted the use of palladium only and hybrid-palladium catalytic converters by most of the major automobile manufacturers. Along with hydrocarbons, it is also important to understand the interaction of NO_x with the palladium catalysts. With the more stringent regula-

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tions that limit the NO_x emissions (1998 low emission vehicle (LEV) NO_x limits for medium duty vehicles were decreased to 0.6 g/mile from the 1997 limit of 1.1 g/mile [11]), palladium catalysts are likely to continue attracting interest in this area. Stationary engines and boilers also represent potential applications for the use of Pd catalysts for reduction of NO_x using hydrocarbons. This continuing interest and their potential warrant an in-depth look into the capabilities of palladium catalysts to reduce NO_x.

It is of great importance to study the interaction of hydrocarbons and NO_x with the palladium surface in different environments. Detailed pre- and post-reaction characterization studies are essential for understanding the nature of the catalyst surface. In our previous studies, we have reported that NO could be effectively reduced by CH_4 over Pd/titania catalysts [12–14]. We have investigated the effect of oxygen concentration and temperature on the kinetics of the reaction. We have also examined this reaction using isotopic tracers. The kinetics of the NO–CH_4 reaction was studied in the presence of oxygen at 500°C, 550°C and 600°C. At each of these temperatures, above a certain critical oxygen concentration in the gas phase, regular, self-sustained oscillations were observed in the product and reactant profiles. Based on these studies, it was concluded that a cyclic phase change from Pd to PdO under certain conditions was possible and these phase changes were responsible for the oscillations in the activity and selectivity of the catalyst. N_2 was primarily a product of NO–CH_4 interaction through a dinitrosyl type surface intermediate while N_2O was thought to be a product of a dimer species. In this article, we report characterization and thermal analysis studies over the Pd/titania catalysts in order to get an insight into the mechanism of NO reduction reaction using methane as a reducing agent.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst used in this study was 2%(wt) Pd/TiO_2 which was prepared using a wet impregnation technique. The TiO_2 (anatase) (Aldrich) support was wet impregnated with a solution of Pd-acetate (Aldrich). Oxalic acid was added to the solution to maintain the pH around 4.0. The solution was then stirred at 90°C for 4.5 h, followed by overnight drying of the slurry in the oven at 100°C. The resulting catalyst was then calcined at 600°C in oxygen for 5 h.

The catalyst used in this study was characterized using several techniques such as BET surface area measurements, scanning electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and laser Raman spectroscopy. The specific surface area of the catalyst was measured using the BET technique with a Micromeritics 2100E Accusorb instrument. The catalyst had a surface area of 12.0 m^2/g. X-ray powder diffraction patterns were obtained using a Scintag PAD-V diffractometer. CuK_α radiation (λ=1.5432 Å) was used as the incident X-ray source. The surface morphology of the catalyst was examined using a Philips XL-30 Field Emission Scanning Electron Microscope, which has a light element X-ray detector. Images were obtained using a voltage of 15 kV and a magnification ranging from 100X to 80 000X. X-ray analysis was performed using a voltage of 30 kV. X-ray photoelectron spectra of the catalysts were obtained using a Physical Electronics/Perkin Elmer (Model 550) ESCA/Auger spectrometer, operated at 15 kV and 20 mA. The X-ray source was Mg K_α radiation (1253.6 eV). The binding energy of C 1s (284.6 eV) was used as a reference in these measurements. The Raman spectra for the catalysts were obtained by using either a double monochromator (SPEX 1403 Ramalog 9-I Spectrometer) or a Triplemate Raman spectrometer (SPEX 1877) which used a charge coupled device (CCD) detector. Both spectrometers use 5 W argon ion lasers (Spectra Physics, model 2016 and 2017, respectively) as excitation source. Catalyst characterization was performed after the initial calcination, after the pre-reduction step, as well as following the reaction.

2.2. Temperature-programmed reduction and desorption

The system used for temperature-programmed studies has been described in detail earlier [9]. A U-shaped quartz cell measured 6 mm OD, 4 mm ID was used as the sample chamber. The temperature-programmed reduction (TPR) experiments were performed with H_2 as a reducing agent. The catalyst was calcined in situ prior to the TPR experiment in an oxygen stream at 500°C, followed by degassing under vacuum at 200°C for 2 h. Hydrogen flow rate over the catalyst was kept at 60 cm^3(STP)/min for the duration of the temperature program, which included an isothermal stage of 30 min at 5°C followed by a temperature ramp up to 900°C at a rate of 10°C/min. The temperature was maintained at 900°C for 20 min. TPR experiments were performed over pre-reduced as well as fully oxidized catalysts. The pre-reduction step was carried out at 200°C with hydrogen, following the in situ calcination and degassing steps. The catalyst was then flushed with He for 1 h at 200°C prior to the beginning of the experiment.

Temperature-programmed desorption (TPD) was performed using NO, CH_4 and H_2O as the adsorbate gas. The amount of catalyst used was 200 mg for these experiments. Before the experiment, the catalyst sample was calcined in situ under an oxygen flow at 500°C for 1 h and then degassed for 2 h at 200°C to remove all the surface species adsorbed due to exposure to ambient air. The adsorption of a specific gas was carried out at room temperature for 2 h. The catalyst was then flushed with helium for 1 h at room temperature to remove all the physically adsorbed species. The heating rate was maintained at 10°C/min. The final temperature reached was 680°C. The catalyst was maintained at the final temperature for 30 min. The gases desorbing from the surface of the catalyst were analyzed either by a thermal conductivity detector (TCD) (Gow-Mac Instrument Company) or a gas chromatograph mass spectrometer (Hewlett-Packard, MS Engine, 5959A) or both. In a separate experiment, the catalyst was also subjected to a temperature program similar to the TPD experiment, without the adsorption of any gases. The same experiment was repeated with the pre-reduced catalyst. Helium was used as the carrier gas for all the temperature-programmed experiments. The flow rate of helium was maintained at 50 cm^3(STP)/min.

3. Results

The catalyst used in this study was palladium supported on titania (anatase). The surface area of the catalyst was 12 m^2/g, which did not show a significant change from that of the support. In the absence of oxygen, methane was able to reduce nitric oxide throughout the temperature range investigated in this study (200–500°C). From 200°C to 300°C, the conversion levels were of the order 10–15%, whereas at 350°C, the conversion level rose all the way to 100% and remained there at higher temperatures used [12]. NO reduction was also investigated in the presence of oxygen at temperatures 500°C, 550°C and 600°C. At each of these temperatures, below a certain oxygen concentration in the gas phase, 100% NO conversion was obtained. If the oxygen concentration was increased beyond this value, an oscillatory behavior was displayed by the system. Isotopic labeling studies in the non-oscillatory range of the reaction have indicated that N_2 and N_2O formations follow different reaction paths. N_2O is primarily viewed as a decomposition product whereas N_2 is viewed as a CH_4/NO interaction product [13].

3.1. Catalyst characterization

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) studies over the oxidized catalysts have shown that all the palladium on the surface is in the form of palladium oxide (PdO), following the synthesis. The XRD pattern of a freshly calcined catalyst is presented in Fig. 1(a). All the features on this XRD pattern corresponds to the anatase phase of TiO_2, with the exception of a weak signal observed at a d spacing of 2.644 Å, which corresponds to the (1 0 1) reflection of PdO. The signal was very weak since the metal loading was quite low for the sensitivity limits of this technique. The powder diffraction pattern of the catalyst which was treated with hydrogen at 200°C for 30 min (Fig. 1(b)) showed, in addition to the peaks that were typical of TiO_2, also a small feature at a d spacing of 2.246 Å, which corresponds to the (1 0 0) reflection of metallic palladium.

The X-ray photoelectron spectra clearly showed that all the palladium present on the surface of a fresh catalyst is in the form of PdO (Fig. 2(a)). Surface characterization was also performed using a controlled-atmosphere chamber after the reduction of the catalyst with hydrogen at 200°C for 30 min. XPS results from this catalyst showed that most of the palladium on the surface was reduced to metallic palladium (Pd^0). Only around 10.5% of the palladium was now in the form of PdO, whereas rest was in the form of metallic palladium (Fig. 2(b)).

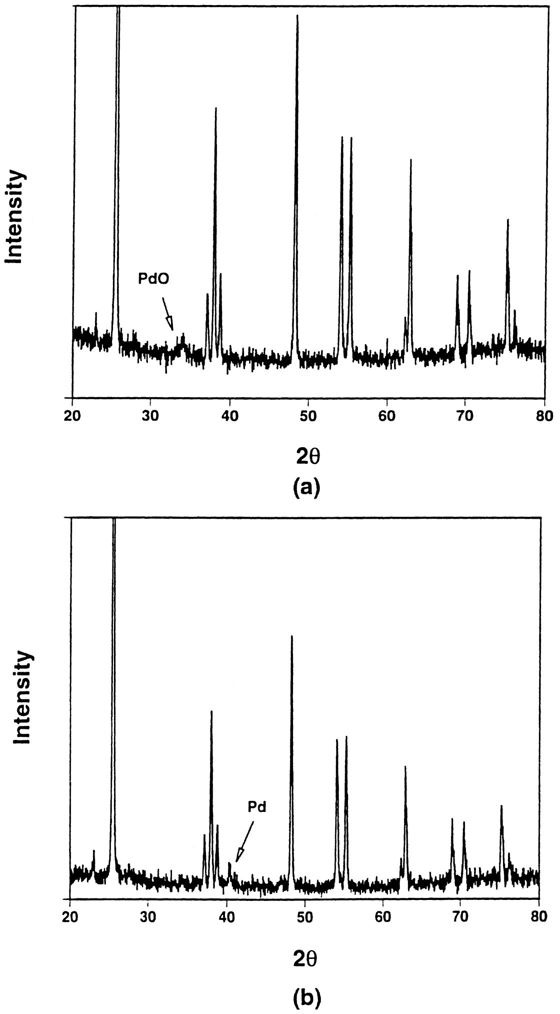


Fig. 1. X-ray diffraction patterns for: (a) oxidized and (b) pre-reduced Pd/TiO_2 catalysts.

Post-reaction XPS analysis of the catalysts was also performed using the controlled-atmosphere chamber. Fig. 2(c) shows the X-ray photoelectron spectrum of a catalyst sample after it was exposed to the $NO+CH_4+O_2$ reaction medium at 500°C for 6 h. The feed mixture used in this experiment contained 1780 ppm NO, 2.12% CH_4 and 2100 ppm oxygen. It was observed that about 58% of the palladium on the surface was in the form of metallic Pd with the rest being PdO.

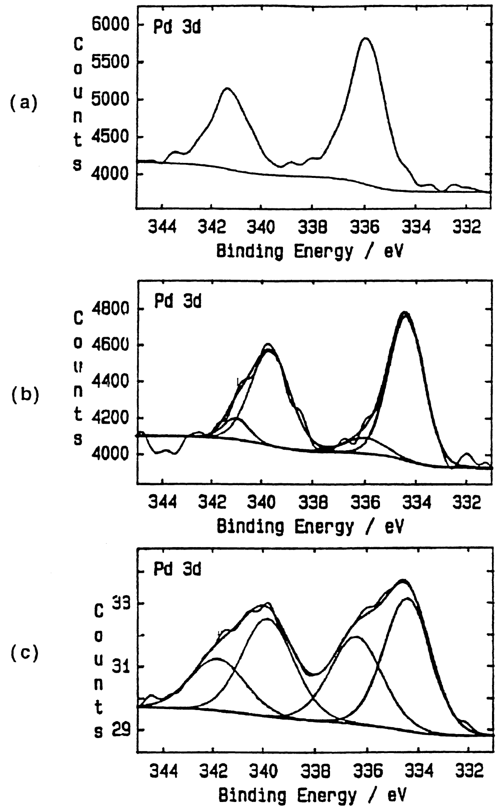


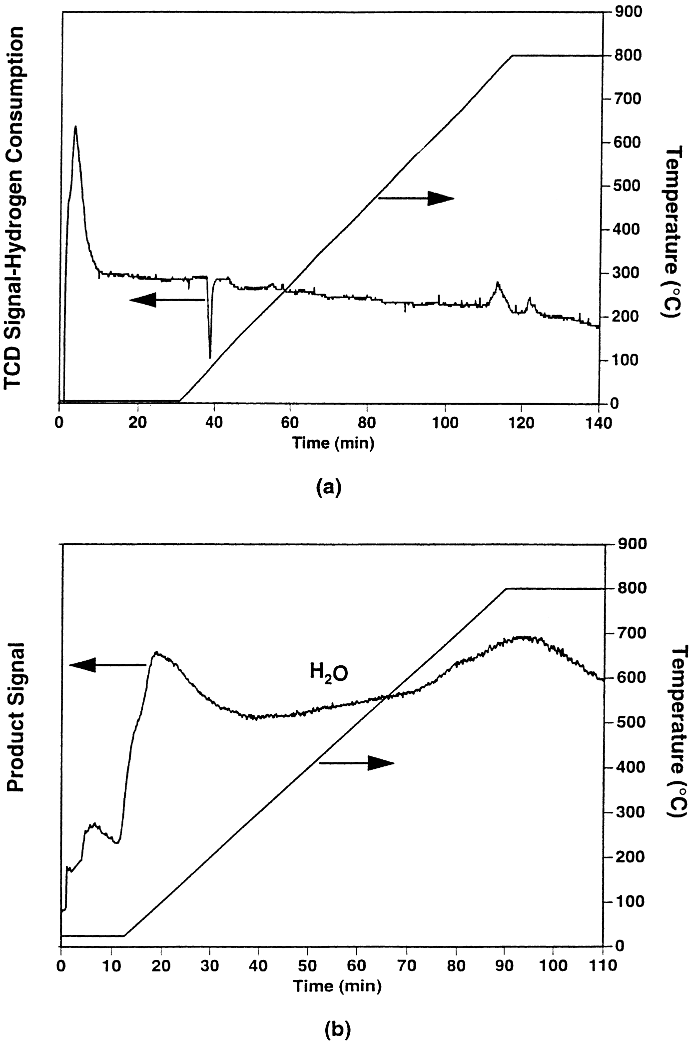
Fig. 2. X-ray photoelectron spectra for: (a) oxidized, (b) pre-reduced and (c) post-reaction (NO=1780 ppm, CH_4=2.12%, O_2=2100 ppm) Pd/TiO_2 catalysts.

The laser Raman characterization of the oxidized and reduced catalyst samples gave spectra essentially identical to the spectrum of the bare support since the characteristic 640–650 cm^{-1} band expected for PdO overlapped with the very strong 635 cm^{-1} band of TiO_2. Hence, it was not possible to observe the presence of PdO on this support material.

Scanning electron microscopy studies done over bare TiO_2 support, which was processed through the same procedure as the catalyst itself, showed uniform spherical particles in the 200 nm size range. The SEM images obtained from the catalyst samples showed similar size and shape of particles. The energy dispersive X-ray analysis did not show any variation in the distribution of Pd signal on the particle surfaces.

3.2. *Temperature-programmed studies*

Temperature-programmed reduction (TPR) experiments over the oxidized as well as pre-reduced catalysts were performed using H_2 as a reducing



(a)

(b)

Fig. 3. Temperature-programmed reduction profiles of oxidized Pd/TiO_2: (a) H_2 consumption (TCD) profile and (b) H_2O profile.

agent. Over the oxidized catalyst, there was a strong hydrogen consumption peak observed while the temperature of the catalyst was kept constant at 5°C (Fig. 3(a)). This indicated that the catalyst can be reduced even at subambient temperatures by H_2. This feature was followed by a hydrogen evolution peak (negative peak) seen at around 95°C. Evolution of H_2 from the surface indicates that H_2 can be adsorbed/dissolved in the surface/subsurface at subambient temperatures and can be released as molecular hydrogen when the catalyst temperature is raised to 95°C. The formation of a hydride followed by its decomposition is also a possibility. Two more smaller hydrogen consumption peaks were seen around 800°C.

When water evolution was monitored over this catalyst using an on-line mass spectrometer in a similar experiment, there were three maxima observed (Fig. 3(b)). One feature was seen at room temperature while the second feature was observed at around 100°C. The second H_2O feature roughly corresponded to the H_2 evolution peak. The third feature observed was above 800°C.

TPR studies were also performed over the pre-reduced catalyst. The catalyst was treated in hydrogen at 200°C for 30 min followed by flushing with helium for 1 h at 200°C. The catalyst was then subjected to a temperature program from room temperature to 800°C at a rate of 10°C/min in a flow of helium. It was then cooled down to room temperature and was later subjected to TPR with hydrogen as in the previous experiment. In this TPR experiment there were four water features observed (Fig. 4). The first feature, which was quite weak, was observed at room temperature. There were three other strong features observed at higher temperatures namely, 400°C, 600°C and 800°C.

As a control experiment, hydrogen TPR was also performed over the bare titania support. Bare titania, when subjected to a similar H_2 TPR procedure, did not appear to reduce at all under the present reaction conditions. This indicates that Pd/titania system shows major differences in the reduction characteristics when compared to bare titania.

Temperature-programmed desorption (TPD) experiment was performed after water adsorption over the catalyst (Fig. 5). The purpose of this experiment was to determine whether the water observed in the H_2 TPR experiment was a product of reaction of H_2 with surface oxygen or it was due to desorption of water which was formed/adsorbed on the surface at lower temperatures. Two distinct H_2O desorption features were observed at 200°C and 500°C. A broad feature was also seen around 600–650°C. It is important to note that none of these peaks coincide with the H_2O signals observed in the H_2 TPR profiles. This indicates that the H_2O peaks observed in H_2 TPR experiments are associated with the reaction of H_2 with the surface oxygen. A strong O_2 feature was also observed at around 680°C. Similar O_2 desorption features were observed when TPD studies were performed after CH_4 and NO adsorption.

Temperature-programmed studies over Pd/TiO_2 catalyst were also performed without adsorption of any gases. The same temperature program as in water TPD experiments was used for this experiment. When Pd/TiO_2 catalyst was subjected to a temperature program without adsorption of any gas, there was a very strong oxygen feature observed at around 680°C. A similar experiment was performed over the pre-reduced catalyst as well. A similar oxygen peak,

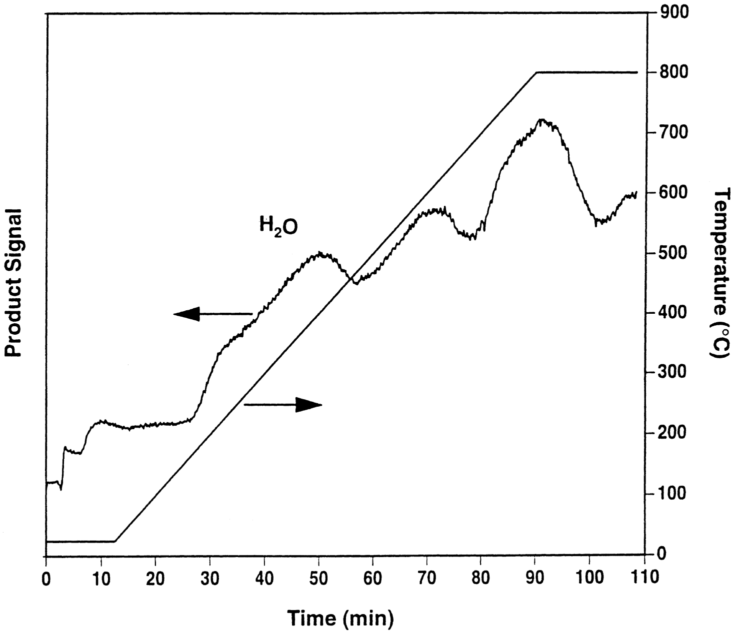


Fig. 4. Temperature-programmed reduction of pre-reduced Pd/TiO_2 catalyst with hydrogen (H_2O profile).

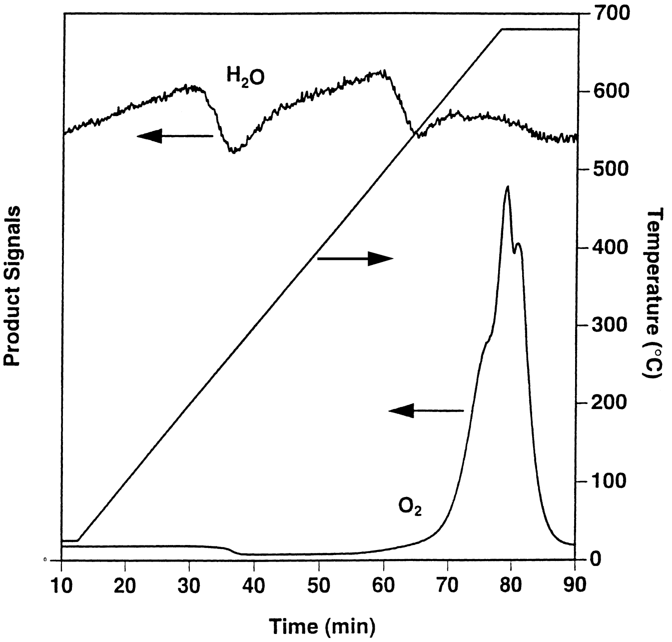


Fig. 5. Temperature-programmed desorption profiles following water adsorption over Pd/TiO$_2$ catalysts.

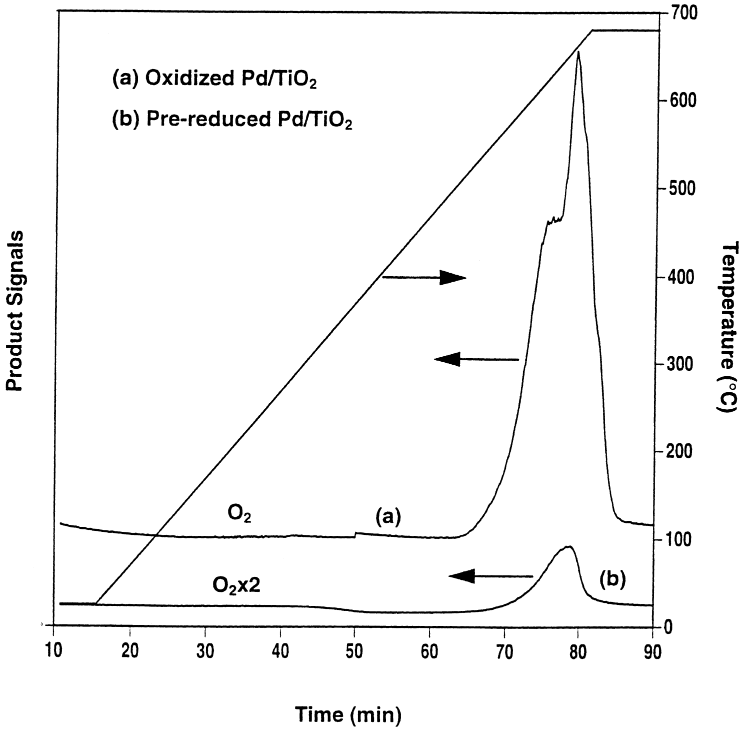


Fig. 6. Blank temperature-programmed desorption profiles of Pd/TiO$_2$ catalysts.

although much weaker in intensity, was observed at around 680°C. The oxygen features observed in these two experiments are shown in Fig. 6.

TPD was also performed following the adsorption of reactants, CH_4 and NO, over the pre-reduced catalysts. These studies were of special significance since the catalyst used in NO reduction reaction with methane was pre-reduced with hydrogen as well, and the knowledge of the adsorption–desorption characteristics of a pre-reduced catalyst was necessary to help explain the reaction behavior of the catalyst.

The results of methane TPD over the pre-reduced catalyst are presented in Fig. 7. The most important observation was that methane adsorbed at room temperature on a pre-reduced catalyst was capable of reacting with the surface as the temperature of the catalyst was increased. CH_4, CO_2 and CO were the three species observed coming off the surface as the temperature of the catalyst was increased. There was one methane desorption feature observed at around 300°C, with a weak shoulder on the low-temperature end. There were two strong features observed in the CO_2 desorption profile. The first feature was observed at 200°C and the second feature at 500°C. The high-temperature feature was much more pronounced than the low-temperature one. There was a shoulder observed for the high-temperature feature at the higher temperature end. Another important observation was the occurrence of a strong carbon monoxide signal at around 400°C. No oxygen desorption was observed in this experiment.

A similar TPD experiment was performed over the pre-reduced catalyst after room temperature adsorption of nitric oxide. The results from this experiment are presented in Fig. 8. NO, N_2O and O_2 were the three species detected coming off the surface as the temperature of the catalyst was increased. Two strong NO desorption features were observed in the 100–450°C range, indicating that NO is reversibly adsorbed on the reduced catalyst surface. A N_2O desorption profile was observed which corresponded to the second desorption feature of NO. Another important observation was the presence of an oxygen desorption feature at around 680°C. This feature was the same as the one observed when the fresh catalyst was sub-

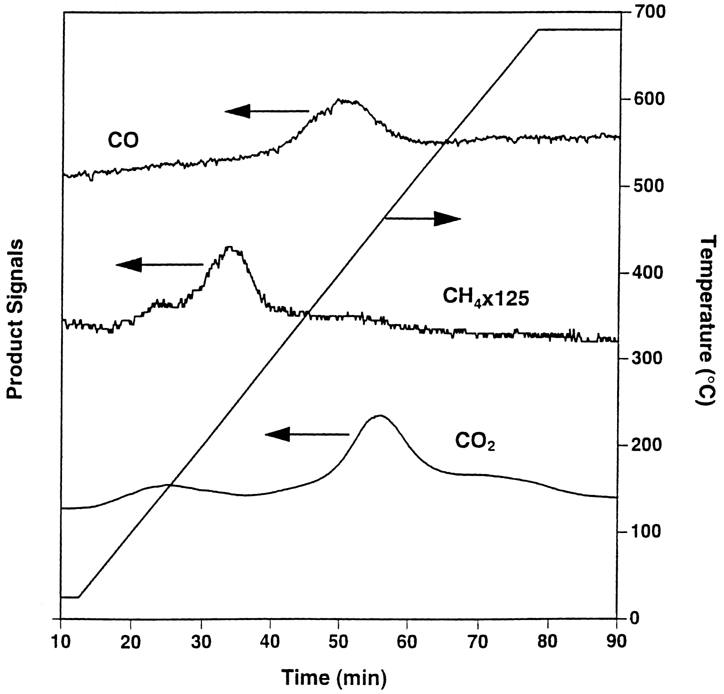


Fig. 7. Temperature-programmed desorption of methane over pre-reduced Pd/TiO_2.

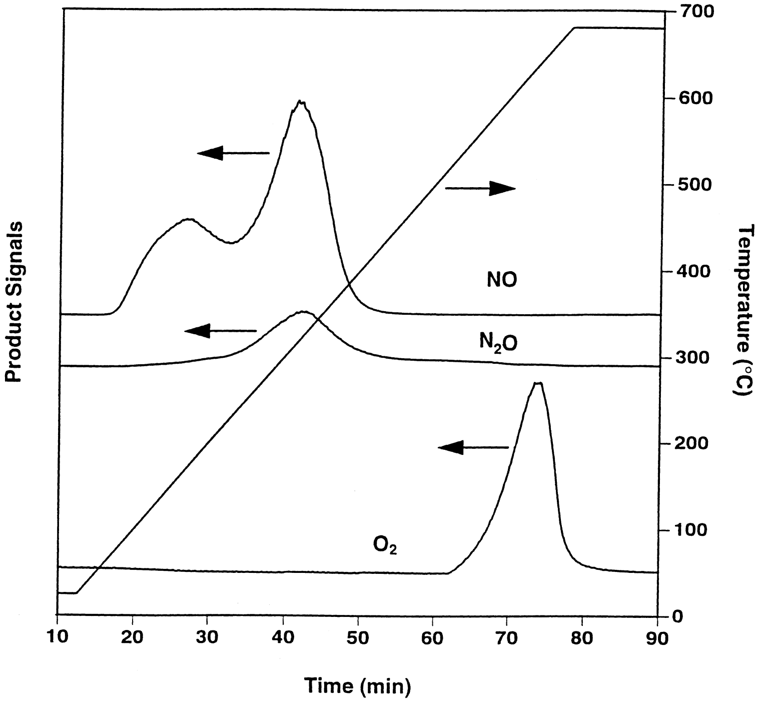


Fig. 8. Temperature-programmed desorption of nitric oxide over pre-reduced Pd/TiO_2.

jected to a temperature program after NO adsorption, CH_4 adsorption, and in a blank TPD experiment.

4. Discussion

In our earlier studies, it was shown that Pd/TiO_2 catalysts can reduce NO in the absence as well as in the presence of oxygen [12]. It was suggested that the reaction network included NO/CH_4 reaction, direct NO decomposition and methane combustion. The extent of each of these reactions appears to be determined by the relative abundance of the oxidic and metallic sites of palladium. The transformation of the sites between the two oxidation states seems to be very fast and driven by the temperature and the oxygen concentration in the medium. Self-sustained oscillatory behavior of the reaction was observed under certain conditions indicating the ease with which the phase transition can take place [14]. It was also concluded that the metallic phase of palladium supported the NO/CH_4 reaction leading to N_2 formation whereas the oxidic phase supported the direct methane oxidation with oxygen and NO decomposition reactions. The isotopic labeling experiments performed have also provided valuable clues regarding the interaction of NO and CH_4 with the Pd/TiO_2 surfaces [13]. These studies have given evidence of the formation of CH_x groups, which are thought to be the major surface species in NO reduction to nitrogen, possibly through the formation of a methyl dinitrosyl-type intermediate. These studies have also provided some indirect evidence of a dimeric species forming over the catalysts and leading to N_2O formation. While CO_2 is thought to be the primary carbon oxide forming from decomposition of the methyl dinitrosyl-type intermediate, CO is likely to be formed as a first step of CH_4 combustion over the oxide sites and to be further oxidized to CO_2, if there is enough oxygen available.

The NO–CH_4 reaction studies performed over Pd/TiO_2 catalysts [12,13], when combined with characterization results, strongly suggest that the phase transition between the oxide and the metallic forms of palladium is critical in determining the catalytic activity of these catalysts in NO reduction reaction. The XRD pattern of the freshly synthesized catalyst indicated that palladium was predominantly in the form of PdO on the titania surface. The (1 0 1) reflection signal, however weak, showed a long-range order of the oxide phase. The XPS results, which showed primarily the Pd^{2+} signal over the freshly synthesized catalyst, were in agreement with these observations. The catalyst samples which were reduced in hydrogen at 200°C for 30 min showed only the metallic palladium on the surface in their XRD patterns. When the same samples were examined by XPS, they showed about 10% of the palladium to be in the oxide form. Since the XPS data were obtained using a controlled-atmosphere chamber, partial reoxidation of the sample by atmospheric oxygen is ruled out as a possibility. Other possible explanations for this observation are an incomplete reduction of the palladium oxide during the hydrogen treatment step or a partial reoxidation of the metallic palladium by oxygen diffusion from the support.

TPR experiments over the oxidized sample showed a hydrogen consumption feature coupled with water evolution at subambient temperatures, indicating the ease of reducing palladium oxide to metallic form. A negative hydrogen peak was observed around 90°C signaling the evolution of hydrogen from the sample. It is likely that a palladium hydride phase is formed at lower temperatures during the hydrogen treatment and the hydrogen evolution corresponds to decomposition of this hydride phase. There exist several reports in the literature [15–18], describing the kinetics and thermodynamics of palladium hydride formation and decomposition as a function of temperature and hydrogen partial pressure. Based on these reports, one would expect the hydride phase to have decomposed completely before the catalyst pretreatment is completed prior to any reaction experiments.

Another interesting observation from the TPR experiment is that there is a high-temperature feature around 800°C. At this temperature, one would expect the palladium to have reduced to metallic form completely. The high-temperature feature is most likely due to oxygen from the titania support which could have been ‘‘mobilized’’ through the interaction with the precious metal. Similar TPR experiments performed on blank titania did not show any reducibility of the support in the 25–900°C range when it did not have the precious metal loading. Increased lability of surface oxygen from the titania surface, when the surface is impregnated with some precious metals, has been reported in the literature earlier [19–22] and remains as a possibility in this case. The TPR results obtained from the freshly oxidized catalyst, when considered alone, cannot provide enough information to determine whether the oxygen from the titania is directly involved in the reduction process or whether it is an indirect involvement in the form of partial reoxidation of palladium to palladium oxide. When one considers the TPR profile from the pre-reduced catalyst, however, it appears more likely that both processes are in operation, since the profile shows two new reduction features at lower temperatures as well as the high-temperature feature around 800°C.

The oxygen signal observed, when the oxidized sample is subjected to a TPD procedure without adsorbing any gases over it, is due to thermal decomposition of the palladium oxide to metallic palladium. Similar behavior is observed when Pd is supported over other oxides [23]. The phase transition takes place at higher temperatures as the partial pressure of oxygen is increased and in some cases shows a hysteresis when the steps are reversed [24]. When the same experiment was repeated over a pre-reduced catalyst, an oxygen signal was observed at exactly the same temperature, but with a much lower intensity, again showing the presence of a small amount of the oxide phase over the pre-reduced catalyst. The fact that it is possible to reduce the PdO even at subambient temperatures leads us to suspect that the pre-reduction process is sufficient to convert all of the oxide to the metallic palladium, however, partial reoxidation takes place through migration of oxygen from the support. Some of our later studies conducted using thermal gravimetric analysis (TGA) and controlled-atmosphere XRD techniques, which showed the relative ease and speed with which the phase transformation, can take place between the oxidic and the metallic phases, lend further support to this suggestion [14].

5. Interaction of NO with Pd/TiO_2 surfaces

Nitric oxide adsorption on various noble metals, including Pd-based catalysts [25–27], has been a topic of intense research mainly because of the environmental issues concerning NO_x and the use of noble metals in the automobile converters. In this study, TPD experiments followed after NO adsorption over a pre-reduced catalyst gave NO, N_2O and O_2 as desorption products (Fig. 8). One obvious conclusion from this experiment is that NO is capable of interacting with the reduced catalyst surface at room temperature. The NO desorption profiles indicate the presence of reversibly adsorbed NO which can desorb from the surface in the low-temperature region (100–200°C) as well as in the mid-temperature region (300–400°C). The two distinct features in the NO desorption profile suggest that there are at least two types of sites available for NO adsorption. The presence of two types of adsorbed NO species over Pd-catalysts has been reported in the literature earlier [27] and these have been proposed to be monomeric and dimeric NO adsorbed species. In our TPD experiment performed following NO adsorption, a distinct N_2O desorption feature was observed which corresponded to the high-temperature desorption feature of NO. This indicates that, of the two types of NO adsorption sites, only one type of site is associated with the formation of N_2O. This observation, combined with the HREELS evidence presented in the literature [27], leads us to suggest that it is a dimeric intermediate which leads to the formation of N_2O molecule. Also, the fact that the N_2O peak corresponds to the high-temperature feature of the two NO desorption peaks suggests a stronger attachment and possibly a longer surface residency for the dimeric species. The oxygen feature observed in the same experiment at around 680°C is very similar to the one observed over the catalyst subjected to a temperature program without any gas adsorption or over the oxidized catalyst and it corresponds to the thermal decomposition of the PdO phase to metallic palladium and gas-phase oxygen. The differences in the intensity are determined by the degree of reduction of the catalyst.

When a similar TPD experiment was performed over a freshly oxidized catalyst, the NO and O_2 desorption profiles obtained [28] were almost identical to those observed over the pre-reduced catalyst. Differences were observed only in the N_2O desorption profile such that, over the oxidized catalyst, there were two additional N_2O peaks at 450°C and 600°C. This may be significant in demonstrating the formation of N_2O and the presence of additional sites that lead to N_2O formation over the oxidized surface as compared to the reduced catalyst.

TPD experiments performed over bare titania support following NO adsorption showed only NO desorbing from the surface with a single feature appearing at around 600°C [29]. This finding, while indicating that NO can adsorb reversibly over bare titania, also pointed out that the titania sites responsible for NO adsorption are possibly blocked by the impregnation of palladium on the surface and do not play a role in this case since the desorption profiles observed over untreated [28] as well as pre-reduced Pd/TiO_2 catalyst exhibited no features around 600°C.

5.1. *Interaction of* CH_4 *with* Pd/TiO_2 *surfaces*

Methane adsorption and reaction over palladium catalysts has been studied in the literature extensively [30–35]. In this study, when a TPD experiment was performed over the pre-reduced catalyst which has been exposed to CH_4 at room temperature, CO, CO_2 and CH_4 were seen to desorb from the surface, showing that methane can adsorb/dissociate as well as oxidize to carbon oxides on the surface. Palladium catalysts are well-known for their methane activation capabilities in oxidation reactions. Decomposition of methane leading to CH_x species has been discussed in detail by Solymosi et al. [36] and Solymosi [37]. The TPD profiles show a methane signal around 300°C followed by CO and CO_2 signals in the 450–500°C range. It is possible that the methane desorption is due to reversible adsorption of methane while the CO and CO_2 signals may be due to dissociative adsorption of methane leading to CH_x (s) and H (s) species on the surface. The fact that there is a broad water signal accompanying these peaks suggests that it is not simply carbon deposition on the surface, but the formation of CH_x species that lead to the carbon oxide desorption. It is also possible that the methane desorption feature is a result of the CH_x species combining with the hydrogen species on the surface before desorbing, as described earlier [36]. The relatively high temperatures at which the carbon oxides desorb from the surface also point out the stability of CH_x species on the surface. When a similar TPD experiment was performed over a bare titania support, no desorption products were observed, demonstrating that the methane activation step is not related to titania, but is strictly a function of the Pd sites.

6. Conclusions

The characterization results described in this article when combined with our reaction and isotopic labeling results lead us to suggest that it is indeed the phase transition which controls the activity and selectivity of the Pd/TiO_2 catalyst in NO reduction reaction. XRD and XPS studies have indicated that a pre-reduced catalyst mainly has metallic Pd sites and as the reaction proceeds one can expect to have a mixture of metallic and oxidic sites, depending on the reaction medium. TPR studies have indicated the ease with which the palladium oxide can be reduced on the surface of titania and the increased mobility of oxygen in titania. NO TPD experiments have clearly indicated that there are at least two types of sites for NO adsorption and the stronger site leads to N_2O formation possibly through a dimer-type species. In conclusion, these characterization and temperature-programmed studies have supported our previously suggested mechanism for the NO reduction reaction that metallic Pd sites promote the NO reduction reaction while the oxidic sites favor the CH_4 oxidation and NO decomposition reactions.

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