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Effect of H_2O and SO_2 on the activity of Pd/TiO_2 catalysts in catalytic reduction of NO with methane in the presence of oxygen

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Abstract

Effect of H_2O and SO_2 on the NO reduction activity of the Pd/titania catalysts was examined in the $NO+CH_4+O_2$ reaction. Steady-state and transient response experiments were performed using a tubular flow reactor. Isotopically labeled methane, $^{13}CH_4$, was used in studying the transient behavior of the catalytic system. Reactor effluents were analyzed by using gas chromatography, mass spectrometry, and chemiluminescense techniques. Steady-state reaction experiments showed that the catalyst has a high activity for reduction of NO over a wide oxygen concentration range (0–9800 ppm at 500°C). Higher N_2 selectivities (less NH_3) and higher methane conversion values were obtained at higher O_2 concentrations. Experiments also showed that NO conversion was not affected by the presence of water (up to 6%), and higher nitrogen selectivities were obtained at higher H_2O concentrations in the feed. On the other hand, significant and irreversible loss of activity was observed in the presence of SO_2. The reaction experiments indicated the formation of SO_3 and H_2S over the catalyst. The post-reaction XPS analysis of the catalyst samples showed that sulfate species were formed on the surface and that the surface palladium was completely converted to Pd^{2+} state after being exposed to SO_2. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; NO reduction; Methane; SO_2; XPS

1. Introduction

Selective catalytic reduction of NO from stationary sources using lower alkanes has been investigated in a large number of studies recently [1–7]. The use of alternative reducing agents such as hydrocarbons is more attractive since the current process which utilizes NH_3 has disadvantages such as corrosion due to ammonium salts, transportation and storage issues. Much attention has been focussed on the use of methane since it is the least expensive lower hydrocarbon, and exists abundantly in natural gas. After the initial work by Iwamoto et al. [7], zeolite catalysts have been the subject of several studies [8–10]. Nishizaka and Misono [11] studied the NO reduction with CH_4 over Pd-H-ZSM-5 and Pd-Ce-H-ZSM-5 in the presence of oxygen, and found that the presence of palladium and protonic acidity was essential for the high SCR activity. Other zeolite catalysts such as Co-ZSM5 have been investigated and it is found that the rate determining step involved a hydrogen abstraction from CH_4 by adsorbed NO_2 , forming methyl species which reacted further with NO [12]. NO reduction over a new family of catalysts, Li-promoted MgO, and rare earth oxides (REO) such as La_2O_3, CeO_2, Nd_2O_3, Sm_2O_3, Tm_2O_3, and Lu_2O_3 was investigated by Zhang

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et al. [13]. It was found that the best REO catalysts were comparable to Co/ZSM-5 on a turn-over frequency basis. The Li-promoted MgO catalysts were also found to be active for NO reduction by CH_4 in the absence of O_2 [14]. Metal ions, Co^{2+}, Mn^{2+}, and Ni^{2+}, exchanged ferrierites were found to be active for NO reduction with CH_4 also [15]. In our earlier studies, we have investigated the use of CH_4 as a reducing agent for selective catalytic reduction of NO over Pd/TiO_2 catalysts in the presence of oxygen [16–19]. The Pd/TiO_2 catalysts were found to give a near complete NO conversion both in the absence and in the presence of oxygen under dry and SO_2 free conditions. The temperature programmed desorption studies and isotopic labeling studies led us to conclude that CH_x groups were formed as a surface species which interact with NO, possibly forming a methyl-dinitrosyl type intermediate to give N_2. The experimental results also suggest that methane combustion yields CO as a primary product, and under excess O_2 conditions, it is further converted to CO_2. We have investigated the effect of oxygen concentration and temperature on the kinetics of the reaction [16]. Our previous studies with isotopic tracers have shown that at certain critical oxygen concentrations at different temperature levels, regular and self-sustained oscillations were observed in both product and reactant profiles. These oscillations were concluded to be the result of cyclic phase transformations from Pd to PdO and were induced by the different levels of exothermicity of the reactions involved [17].

The presence of other constituents from the emissions of stationary and mobile sources such as SO_2 and H_2O requires further examination of the reaction mechanism and catalyst activity. In the literature, different effects of SO_2 and H_2O on NO SCR have been presented. The addition of SO_2 has been reported either to enhance or inhibit the SCR activity. Chen and Yang [20,21] reported that the presence of SO_2 improved the SCR activity over V_2O_5/TiO_2 catalyst due to the increased Brónsted acidity. Moreover, they found that WO_3 promotion on the catalyst increased the SCR activity furthermore.

In a different study, NO reduction by NH_3 on copper ion exchanged H-mordenite catalyst was found to decrease rapidly after SO_2 was introduced in the reactant mixture [22]. Amiridis et al. [23] studied the effect of H_2O and SO_2 on V_2O_5/TiO_2 catalysts and showed that H_2O competitively adsorbed on vanadyl sites against NH_3 and NO. SO_2 was proposed to be responsible for the formation of surface sulfate species.

There have been several reports on the effect of SO_2 on the NO reduction with lower hydrocarbons over different catalysts. Li and Armor [24] investigated the effect of SO_2 on the Co-ZSM-5 and Co-ferrierite for the NO reduction by CH_4 in the presence of O_2. Over BSA (B_2O_3–SiO_2–Al_2O_3) supported platinum catalysts, it has been reported that a 100 ppm of SO_2 improved the SCR activity using propene and depressed the formation of N_2O. The inhibition of N_2O formation was attributed to the retarded mobility of NO by SO_2 [25]. The effect of a residual amount of SO_2 (20 ppm) inhibited NO conversion over alumina with propane; however, its activity quickly returned to normal after removing the SO_2 from the feed. It was concluded that SO_2 and NO competed with each other for the same adsorption sites [26]. Sirilumpen and Yang [27] investigated the NO reduction by ethylene in the presence of oxygen over Cu^{2+} ion-exchanged pillared clays. They reported that the effect of SO_2 was very mild and NO conversion decreased only slightly at 500°C. However, at 350°C, the deactivation was very severe possibly due to competitive adsorption on the active sites. Effect of sulfur and sulfur compounds on the reduction of NO over noble metal automotive catalysts (Pt, Pd, Rd, and Ir on γ-Al_2O_3) under oxidizing and reducing conditions was examined by Gandhi and Shelef [28]. They found that the dispersion of metal particles on support was the important factor on the oxidation of SO_2 and the activity of NO reduction to both dinitrogen and ammonia over the Pt and Pd catalyst was completely suppressed by the presence of very low levels of SO_2. They also concluded that, under oxidizing conditions, sulfur storage capability of the support in the form of sulfate directly affected the poisoning resistance of the catalyst. The sulfation of TiO_2 was studied by Chen and Yang [21] with respect to the SCR of NO with NH_3. In this study SO_4^{-2}/TiO_2 super acid catalyst was obtained as a result of reaction between the SO_2 and TiO_2 under oxidizing conditions. The interaction of SO_2 with Pd film has been investigated in the temperature range -80–250°C by Saleh [29] in the late 1960s. About 20% of total SO_2 adsorbed at -80°C was reversible and 25% of the adsorbed gas desorbed rapidly when the film was heated to 25°C. No further adsorption was observed after that up to 250°C.

As a continuation of our earlier work on NO+CH_4 reaction over Pd/TiO_2 catalysts [16–19], in this study, we examined the effect of SO_2 and H_2O the reduction of NO with CH_4 over the same catalyst system.

2. Experimental

2.1. Catalyst preparation

The catalyst used in this study was 2 wt% Pd/TiO_2 which was prepared using a wet impregnation technique. Palladium acetate (Aldrich) and TiO_2 anatase (Aldrich) were wet-impregnated in either an acetone or an aqueous solution at the boiling point followed by drying in an oven for overnight for the 2 wt% Pd/TiO_2 followed by calcination in an oxygen flow at 500°C for 4 h. The surface areas of the Pd/TiO_2 catalysts prepared by acetone and water solution were 19.1 and 12.0 m^2/g, respectively.

2.2. Catalyst characterization

The catalyst characterization techniques included BET surface area measurements, X-ray photoelectron spectroscopy, X-ray diffraction, temperature-programmed reduction and desorption. The specific surface area of the catalysts used were measured by a Micromeritics 2100 E Accusorb instrument using nitrogen adsorption. The X-ray photoelectron spectrum of post reaction catalysts and oxidized catalysts were obtained by a Physical Electronics/Perkin Elmer (Model 550) ESCA/Auger spectrometer, operated at 15 kV and 20 mA. Mg K_α radiation (1253.6 eV) was used as the X-ray source. The charge shift was corrected using the binding energy of C 1s (284.6 eV) as a reference. A controlled-atmosphere chamber was used for the post-reaction catalyst samples.

2.3. Reaction studies

The steady-state reaction studies were performed in a fixed-bed flow reactor (1/4 in. OD) made of stainless steel. The amount of catalyst used in this study was 37.5 mg. The feed consisted of NO (1780 ppm), CH_4 (2.13%), O_2 (1780 ppm to 9800 ppm), H_2O (0–6%), and SO_2 (0–1780 ppm) in balance He. Since self-induced oscillations were observed at certain oxygen concentration ranges in our earlier study [18], the reaction conditions were chosen to ensure the operation of the system in the oscillation-free regime. The total flow rate was kept at 62 cm^3/min. Water was included into the reactant gas mixture using a syringe pump. All lines containing water were heated at 125°C to prevent the condensation of H_2O. A trap was located at the exit of the reactor to separate possible elemental sulfur product from the product stream. The feed and product streams were analyzed on-line using a combination of a gas chromatograph (GC) (Hewlett Packard 5890A), a chemiluminescence NO–NO_2–NO_x analyzer (Thermo Environmental Instruments, Model 42H), and an IR ammonia analyzer (Siemens Ultramat 5F). The GC was equipped with a 10 ft× 1/8 in. Porapaq Q column and a 8 ft×1/8 in. molecular sieve column to quantify N_2, O_2, CO, CO_2, CH_4, N_2O, and SO_2. The reaction temperature was 500°C which was controlled by a PID temperature controller. The catalyst was pre-reduced in situ in 33% H_2 in He at 30 cm^3/min for 30 min at 200°C followed by flushing with He for 1 h.

2.4. Transient response and isotopically labeled reaction experiments

A 100 mg of Pd/TiO_2 was used for transient response experiments. All transient response and isotopically labeled reaction experiments were carried out in a TPD system connected to GC-MS (HP 5989A). The detailed description of the system can be found elsewhere [30]. The catalysts were first calcined in situ in O_2 flow for 2 h at 500°C and reduced in 33% H_2 in He stream for 30 min at 200°C followed by degassing for 2 h to clean the surface. The catalyst was then heated to the reaction temperature and the mixture of NO, $^{13}CH_4$, O_2, SO_2 , and He were introduced as reaction feed. The transient response experiments were carried out by changing reaction mixture with He, and reaction response was monitored by GC–MS.

3. Results and discussion

The reaction studies were conducted to investigate the effect of other stack gas components, such as H_2O

and SO_2 in the reduction of NO with CH_4 over Pd/TiO_2. A feed stream which contained water vapor was introduced over the catalysts which were prepared in an acetone solution as opposed to an aqueous solution, as reported previously [16]. The difference between the catalyst used in these wet feed experiments and the previous ones arises in the use of different media during impregnation. Our previous studies, which were conducted over Pd/TiO_2 catalysts prepared in aqueous media, have shown to convert over 98% NO at oxygen concentrations between 0 and 2900 ppm at 500°C. At O_2 concentration of 3800 ppm, the oscillatory behavior was observed [18]. With the catalyst prepared in acetone solution, we observed over 98% NO conversion up to O_2 concentrations of 7800 ppm at the same temperature level. The latter preparation also gave a higher surface area. Another difference was that the catalyst prepared in aqueous media gave a higher selectivity to N_2 (>95%). Since the catalyst prepared in acetone remained active over a wider range of O_2 concentration, we have examined the effect of O_2 concentration on the N_2 selectivity over this catalyst. Fig. 1 shows the result of the variation of N_2 selectivity with O_2 concentration level at 500°C. The NO conversion was at 100% and CH_4 conversion increased from 8% at 2100 ppm O_2 concentration to over 20% at 7800 ppm O_2 concentration. In this range, N_2 and NH_3 were the only nitrogen containing products observed. As seen in Fig. 1, with an increase in the O_2 feed concentration, the N_2 selectivity over NH_3 increased steadily under these conditions. The lower ammonia selectivities with increasing oxygen concentration can be due to the formation of H_2O from methane instead of H_2 at higher oxygen concentrations. This, in turn, can reduce the formation rate of NH_3. Another possible explanation is the oxidation of NH_3 itself to NO or to N_2.

At an O_2 concentration of 2100 ppm, the effect of H_2O on NO conversion was investigated. After steady-state was reached with dry feed, 1.87% H_2O was introduced to the feed stream keeping the same total feed flow rate. Experiments were performed with H_2O concentration levels of 4% and 6% also. In these experiments, the nitrogen and carbon containing products observed were N_2, NH_3, and CO_2. The results showed that there was no effect of H_2O on the NO conversion, which remained constant at 99.9%, during the 24 h time-period the catalyst was kept on-stream. Fig. 2 shows the nitrogen selectivity at different H_2O inlet concentrations at 500°C at an O_2 concentration of 2100 ppm. We observed a decrease in NH_3 production rate with an increase in the inlet H_2O concentration, thus increasing the N_2 selectivity. This result may seem surprising if one considers that the presence of water may lead to water gas shift reaction between CO and H_2O or steam reforming reaction between CH_4 and H_2O, both giving rise to H_2 formation. The fact that there was no increase in methane conversion with increasing H_2O concentration suggests that steam reforming of methane does not take place to any appreciable extent under these conditions. These results suggest that either the extent of these reactions

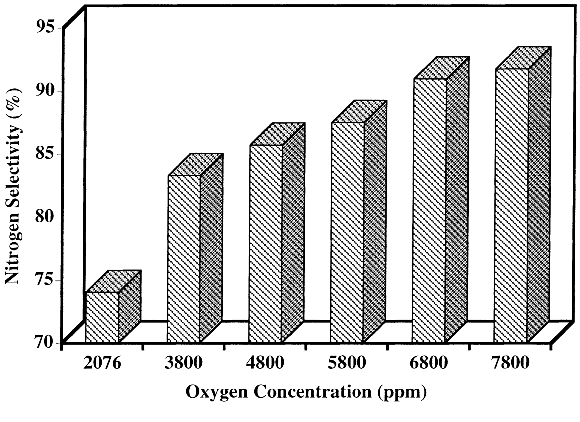

Fig. 1. Variation of nitrogen selectivity with oxygen concentration.

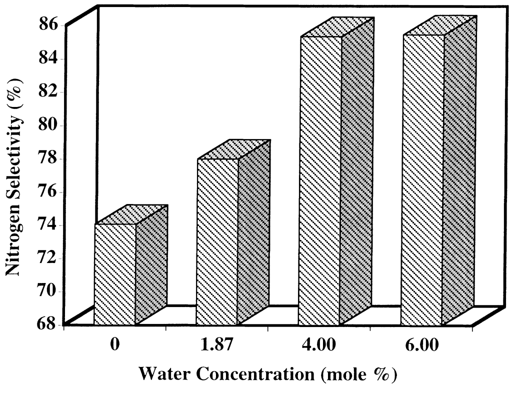

Fig. 2. Variation of nitrogen selectivity with water concentration (NO: 1780 ppm, CH_4: 2.13%, O_2: 2100 ppm, T=500°C).

is negligible or that there are other reactions which affect the NH_3 selectivity more strongly. One such reaction is the reduction of NO with NH_3. However, additional experiments would be needed to determine to what extent this reaction proceeds under the given conditions.

The effect of SO_2 on the NO reduction with CH_4 over Pd/TiO_2 catalysts was investigated by performing a steady-state reaction where a fraction of the O_2 molecules was replaced by SO_2 so that the total O_2+SO_2 concentration was kept constant before and after the addition of SO_2 to distinguish the poisoning effect from surpassing the critical O_2 concentration where the near-complete NO conversion is lost due to the transformation of metallic palladium to PdO. The feed composition before and after the introduction of SO_2 consisted of 1780 ppm NO, 2.13% CH_4, and 2900 ppm O_2, and 1780 ppm NO, 2.13% CH_4, 1758 ppm SO_2, and 1142 ppm O_2, respectively. After obtaining a steady-state and near complete NO conversion in the presence of O_2, SO_2 was added to observe the effect on the catalytic activity. Immediately after the injection of SO_2, NO conversion declined to less than 1% as shown in Fig. 3(a). The result indicated that SO_2 was indeed poisoning the SCR activity. In a separate experiment, the feed concentrations of NO, CH_4 and O_2 were kept constant at 1780 ppm, 2.13%, and 2000 ppm, respectively. After steady-state was established, 178 ppm of SO_2 was included in the feed stream. Even such a low SO_2 concentration led to a significant drop in the NO conversion as seen in Fig. 3(b). Using the same catalyst, we increased the SO_2 concentration to 3516 ppm while keeping the same O_2 concentration. Fig. 3(c) shows that the variation in SO_2 consumption rate is very similar at two different SO_2 concentration levels. An increase in SO_2 concentration did not change its consumption rate significantly.

The reversibility of the effect of SO_2 on Pd/TiO_2 was also examined by simply removing the SO_2 feed after 1 h of SO_2 on stream. The NO conversion did not go back to its pre-SO_2 level, indicating that the poisoning effect was irreversible. Furthermore, the catalysts were subjected to hydrogen reduction for 30 min at 200°C in a stream containing 33% H_2 in helium followed by a regular NO reduction experiment to see the effect of regeneration. The regeneration effort with hydrogen was not effective in bringing back the NO reduction activity, either, suggesting that the loss of activity was not due to a simple phase transformation of the palladium catalyst.

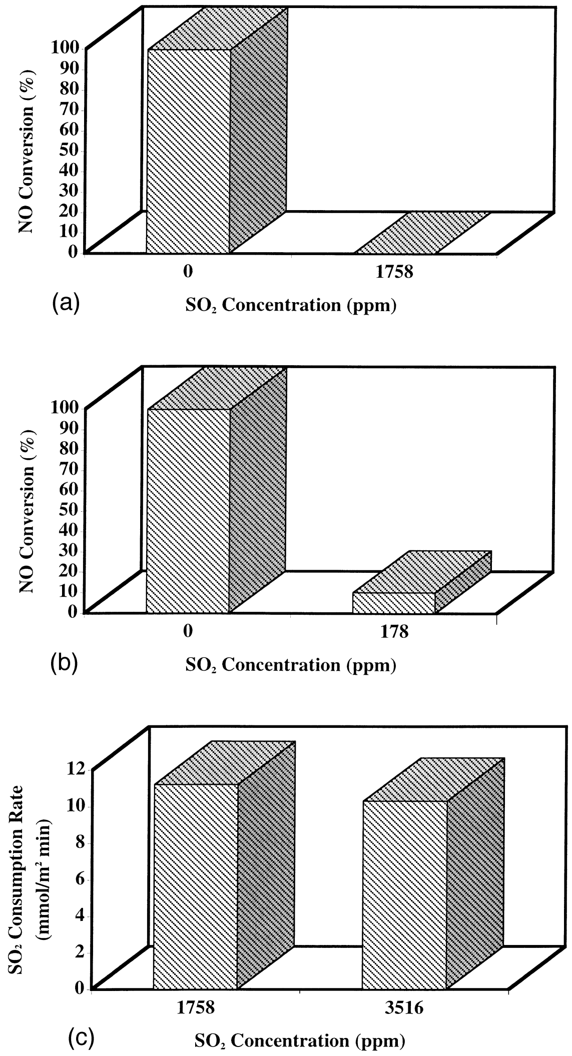

Fig. 3. Effect of SO_2 Concentration in $NO+CH_4+O_2$ reaction: (a) effect of SO_2 feed concentration (1758 ppm) on NO conversion; (b) effect of SO_2 feed concentration (178 ppm) on NO conversion; (c) variation of SO_2 consumption rate with SO_2 feed concentration.

In order to gain a better insight into the type of species formed when SO_2 is incorporated into the feed, steady-state experiments were performed with isotopically labeled $^{13}CH_4$ and the products were analyzed on-line by a gas chromatograph–mass spectrometer. The use of $^{13}CH_4$ was necessary to differentiate between N_2 and CO and between N_2O and CO_2 using the mass spectrometer. The reaction was first brought to steady state without SO_2. At this point, the NO conversion was around 99%. Then SO_2 was introduced to the feed without changing the total flow rate. In addition to the products normally observed in $NO+CH_4+O_2$ reaction, sulfur-containing species, H_2S (34, 33), ^{13}COS (61), $^{13}CS_2$ (77), SO_3 (80), $^{13}CH_2S$ (46, 47) were monitored with *m*/*e* numbers written in parentheses. Right after the SO_2 addition, there was an immediate rise in the NO level and an immediate decline in the N_2 level. The only S-containing products detected were SO_3 and H_2S.

After the steady-state reaction with $NO+{}^{13}CH_4+O_2+SO_2$, the feed mixture was abruptly changed to a He stream to observe the SO_2 and SO_3 transient relaxation. As it is shown in Fig. 4, SO_2 relaxation to zero takes place much more rapidly after the switch while SO_3 relaxation proceeds rather slowly indicating the possible desorption of SO_3 species from the catalyst surface.

The post-reaction Pd/TiO_2 sample which was subjected to the reaction with CH_4, O_2, SO_2, and NO stream for more than 13 h and the oxidized sample were analyzed by X-ray photoelectron spectroscopy. The samples were transferred to the XPS chamber under controlled-atmosphere conditions. Fig. 5 shows the S 2p XPS spectrum with a binding energy of

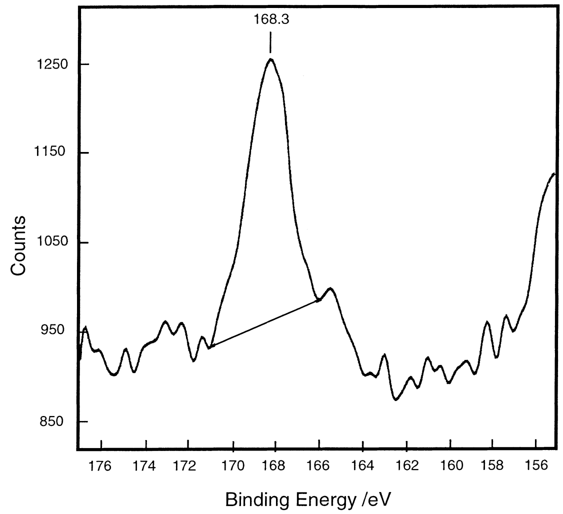

Fig. 5. Post-reaction S 2p XPS Spectrum of Pd/TiO_2 sample ($CH_4+NO+O_2+SO_2$).

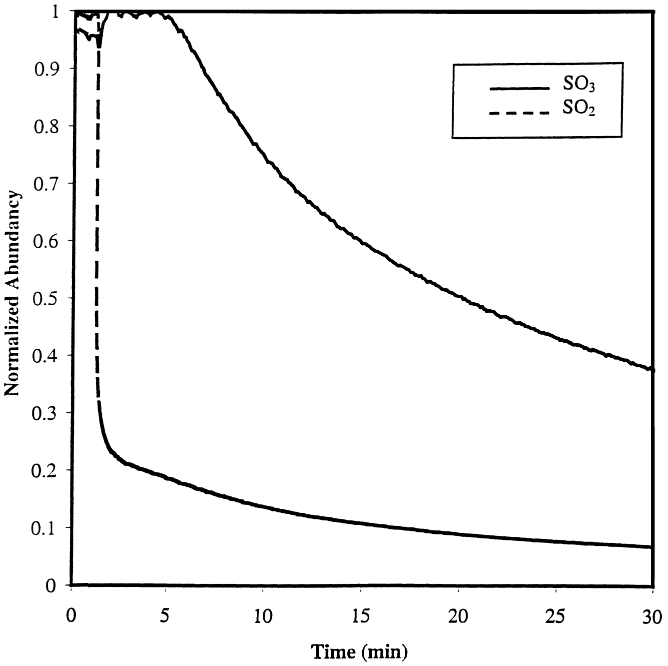

Fig. 4. Transient response of SO_2 and SO_3 after switching from ($NO+{}^{13}CH_4+O_2+SO_2+He$) reaction mixture to He.

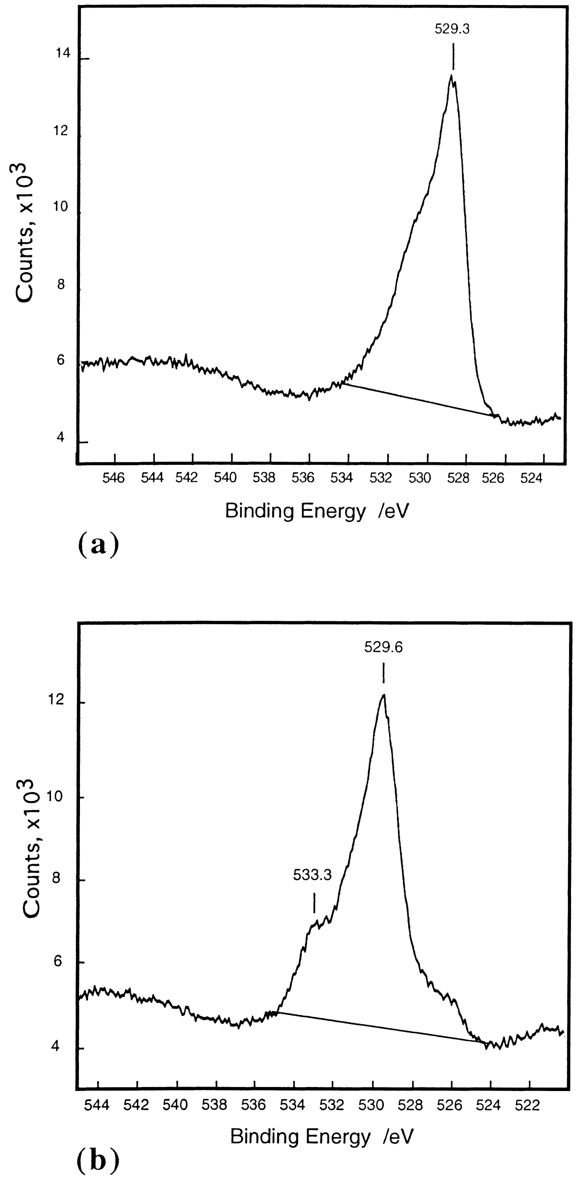

Fig. 6. O 1s XPS Spectra of Pd/TiO_2: (a) oxidized Pd/TiO_2 sample; (b) post-reaction sample (CH_4+NO+O_2+SO_2).

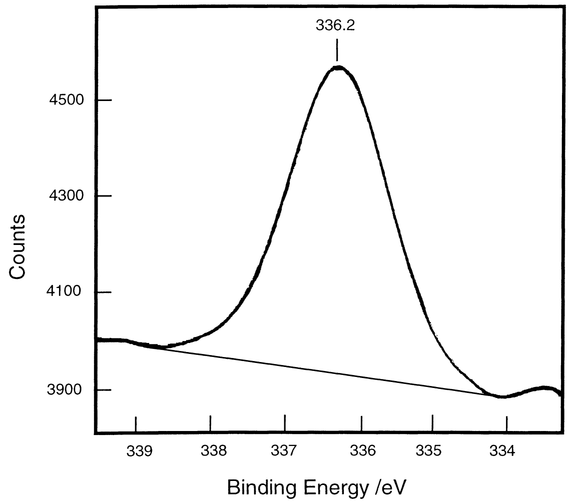

Fig. 7. Post-reaction Pd $3d_{5/2}$ XPS spectrum of Pd/TiO_2 sample (CH_4+NO+O_2+SO_2).

168.3 eV. This spectrum signals the presence of sulfur on the surface as well indicating that it is in the form of a sulfate rather than a sulfide. The O 1s spectra of the oxidized sample and the post-reaction sample are presented in Fig. 6(a) and (b), respectively. In addition to the major peak seen for the oxidized sample at 529.3 eV, the post-reaction sample shows a shoulder at 533.3 eV. This shoulder has been reported to be characteristic of oxygen in sulfates (SO_4, SO_3) [21]. This evidence, combined with the S 2p spectrum, suggests that surface is in a sulfated form.

Fig. 7 shows the Pd $3d_{5/2}$ spectrum obtained from the catalyst after it was exposed to NO+CH_4+O_2+SO_2 reaction medium. It is observed that palladium on the surface is transformed to Pd^{2+} form completely without any metallic palladium left on the surface. This is in clear contrast to our previous XPS studies which have shown that about 60% of the palladium on the surface of the Pd/TiO_2 catalyst which was exposed to the NO+CH_4+O_2 reaction medium at 500°C for 6 h was still in the form of metallic Pd [16].

When we examine the Ti 2p XPS spectrum of the post-reaction sample (Fig. 8), we see no shifts in binding energy. At this point, we cannot rule out the possibility of a sulfate formation associated with the support as well as the palladium sites, since it has been reported that the sulfate groups associated with the Ti centers would not lead to a major shift in the binding energy of Ti from that of unsulfated TiO_2 [21].

4. Summary

The NO+CH_4+O_2 reaction experiments over Pd/TiO_2 catalysts showed that water had no inhibition

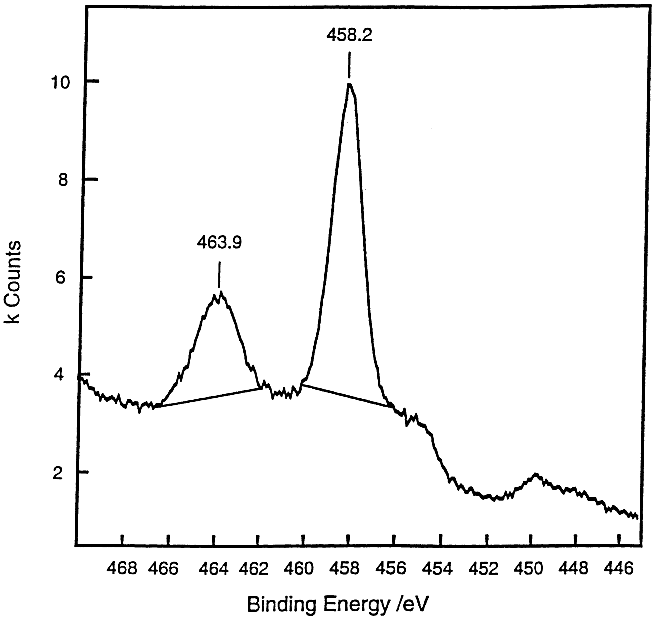

Fig. 8. Post-reaction Ti 2p XPS spectrum of Pd/TiO_2 sample (CH_4+NO+O_2+SO_2).

effect over NO reduction activity, but improved N_2 selectivity. Steady-state and transient response reaction experiments combined with post-reaction characterization studies showed an irreversible inhibition effect of SO_2 on the NO reduction activity of the Pd/TiO_2 catalysts. The post-reaction XPS results that showed that the Ti spectrum remained unchanged as a result of the exposure to SO_2 containing mixture while palladium was completely converted to a Pd^{2+} state. A regeneration effort with hydrogen at 200°C did not reactivate the catalyst, indicating that the change was not simply due to oxidation of the metallic palladium sites to PdO sites. The post-reaction XPS studies of S and O suggested the formation of a sulfate species on the surface. The transient relaxation behavior of SO_3 desorbing from the surface also supported the possibility of a sulfate species formation. Studies are currently underway examining the effect of the palladium dispersion on the resistance of the catalyst to SO_2 poisoning.

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