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Chemisorption of Nitric Oxide on Platinized Titania[1]

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The chemisorption of NO on platinized TiO_2 was studied at 300 K by Fourier transform infrared spectrometry and uptake methods. Two absorption bands at about 1760 and 1700 cm^{-1}, which have been assigned as NO adsorbed on Pt open sites and on close-packed sites, respectively, were found to vary in intensity with reduction and O_2 pretreatment. Nitric oxide uptake is also diminished on reduced, SMSI, Pt/TiO_2. To explain the interaction between Pt and adsorbate, an extended "electronic ligand effect" concept is applied. Both electron transfer from the support to the metal particles and an induced morphology change of the Pt are proposed to interpret the variations of the observed NO absorption bands.

1. INTRODUCTION

There has been recent interest in the catalytic reduction of NO to N_2 without formation of undesirable byproducts, such as NH_3 (*1*). Nitric oxide is also interesting from a chemical point of view because of its wide variety of bonding modes in inorganic complexes (*2*). Since NO and CO have similar molecular orbital structure except that NO has an extra unpaired electron in the antibonding $2\pi^*$ orbital, one expects them to have relatable adsorption behavior.

The uptake of both H_2 and CO on TiO_2-supported transition metal catalysts is strongly diminished by prereduction in H_2 at 500°C (*3*). This characteristic is called the strong metal–support interaction (SMSI) and has been shown to give significant effects in CO hydrogenation activity and selectivity (*4*). In an effort to understand the interaction between the metal and adsorbate which leads to SMSI, we have studied NO adsorption on various forms of Pt/TiO_2. This is part of a continuing effort in our laboratory to characterize the chemisorption and photoassisted catalytic properties of TiO_2-based systems (*5–9*). In this paper we show that the extent of NO adsorption is dramatically reduced when Pt/TiO_2 is in its SMSI state. Thus, the SMSI effect extends to NO chemisorption.

2. EXPERIMENTAL

All the procedures used here for IR experiments are identical to those reported in a previous paper from this laboratory (*6*). Infrared spectra were taken on a Nicolet 7199 FT-IR spectrometer and recorded in absorbance with 2 cm^{-1} resolution. Absorption due to the CaF_2 windows and the gas phase were subtracted. With the exception of Figs. 1a–1c, the pellet backgrounds were also subtracted. All spectra were recorded at room temperature in the presence of gas phase NO (except Fig. 1a). Anatase (MCB) was reduced with H_2 at 800°C and subsequently soaked in dilute chloroplatinic acid (Alpha Products) solution to prepare 2 wt% Pt/TiO_2. The samples were washed with distilled water until no chloride could be detected in the wash water. Such samples are quite dark colored and show relatively high conductivity (*7*) and Ti^{3+} ESR signals (*9*).

A single sample pellet was used for all the ir studies. It was pressed between two pieces of paraffin paper and the thickness was about 25 mg/cm^2; the advantages and disadvantages of this procedure have been

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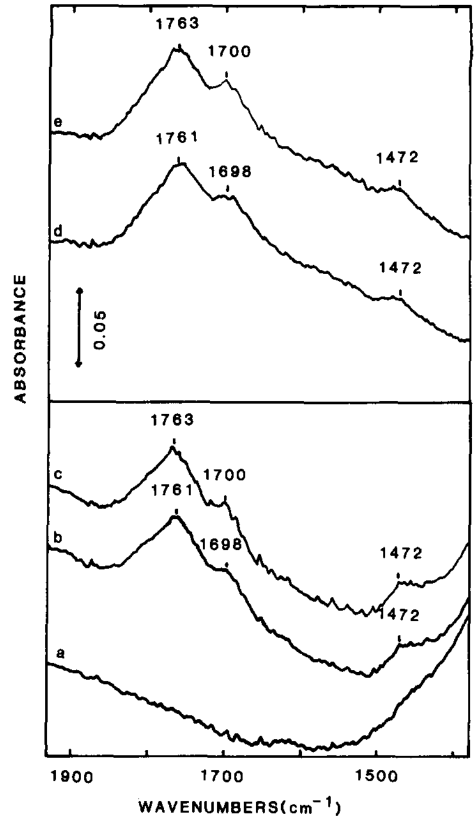

FIG. 1. Infrared spectra of 42 Torr NO adsorbed on Pt/TiO_2 (400–400–400). (a) Background of Pt/TiO_2; (b) 42 Torr NO exposure; (c) after 29 min of exposure to NO; (d) subtraction spectrum, (b)–(a); (e) subtraction spectrum, (c)–(a).

discussed previously (*6*). The pellet was oxidized overnight at 400°C in the ir cell in order to remove paraffin fragments. The experiments were performed in the order given in Section 3, i.e., Fig. 1a first and Fig. 3c last.

The pellet treatment procedure is denoted by three temperatures: (1) the evacuation with/without oxidation, (2) the reduction, and (3) the evacuation temperatures. The oxidation and reduction pressures are about 700 Torr. For example, the notation 400–200–400 signifies (1) evacuation at 400°C for 30 min and oxidation at 400°C overnight, (2) reduction at 200°C, and (3) evacuation at 400°C for 30 min. The notation (400)–500–400 means (1) evacuation at 400°C for 30 min without oxidation, (2) reduction at 500°C, and (3) evacuation at 400°C for 30 min.

Molecular oxygen was used in the oxidation of the sample pellet. It was purified before use by passage through a molecular sieve trap in a liquid nitrogen dewar. Hydrogen was purified through a Pt/Al_2O_3 catalyst at 300°C to convert the O_2 impurity to H_2O, which was then removed by a molecular sieve trap at liquid nitrogen temperature. Nitric oxide was purified by a standard vacuum distillation; dissolved N_2 was removed by a freeze–thaw technique (*10*). ^{15}NO (Stohler Isotope Chemicals, 99% ^{15}N) was used without further purification.

NO uptake studies on four samples (1) SMSI Pt/TiO_2 (*7*), (2) ((400)–200–400) Pt/TiO_2, (3) ((400)–500–400) Pt/TiO_2, and (4) (400–200–400) Pt/TiO_2 samples were performed in a conventional volumetric system described elsewhere (*7*). Except for sample 1 in which the TiO_2 had been reduced in flowing H_2 at 875°C before Pt deposition, all samples were from the same batch as the ir pellet.

3. RESULTS

3.1. NO Adsorption on Pt/TiO_2 (400–400–400)

NO absorption spectra on the Pt/TiO_2 (400–400–400) pellet after a reduction pretreatment in 700 Torr of H_2 overnight at 400°C are shown in Fig. 1. Figure 1a is the spectrum of the pellet before the NO exposure. After 42 Torr NO was introduced (Fig. 1b), two bands at 1761 and 1472 cm^{-1}, and a shoulder at 1698 cm^{-1}, were observed. The 1472 cm^{-1} band was also observed in NO adsorption on TiO_2 and is assigned as an oxidized NO species, possibly adsorbed nitrate. The other two absorption bands at 1761 and 1698 cm^{-1} are assigned as terminal bonded NO on open and close-packed Pt sites, respectively, and will be discussed later. To examine the NO stability on the Pt/TiO_2 surface, a spectrum (Fig. 1c) was recorded after 29 min of NO exposure. There was no significant change, indi-

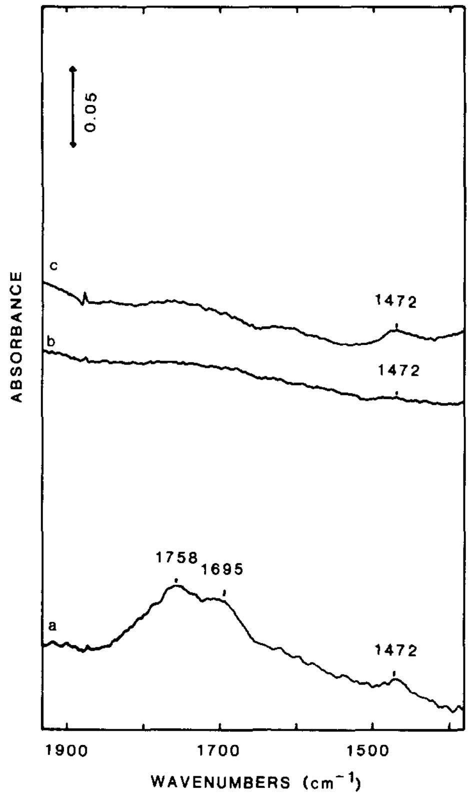

FIG. 2. (a) Infrared spectrum of 38 Torr NO adsorbed on Pt/TiO_2 ((400)–500–400) with H_2 pretreatment at 500°C overnight; and ir spectra of NO adsorbed on Pt/TiO_2 ((400)–500–400) with H_2 pretreatment at 500°C for 4 days; (b) 18 Torr NO exposure; and (c) 60 Torr NO exposure.

cating that NO was quite stable on the Pt/TiO_2 surface during this experimental period. The background subtracted spectra, (b)–(a) and (c)–(a), are shown in Figs. 1d and e, respectively.

3.2. NO Adsorption on Pt/TiO_2 ((400)–500–400)

After finishing the experiment described in Section 3.1, the Pt/TiO_2 pellet was outgassed at 400°C for 30 min. Through this procedure, adsorbed N atoms derived from the dissociation of NO and adsorbed NO molecules should be removed from Pt particles based on the temperature-programmed desorption (TDS) studies on Pt single crystal surfaces (*11–14*). Following this the sample was reduced in 700 Torr of H_2 at 500°C overnight; during this period the H_2 gas in the ir cell was changed three times by evacuation at 400°C for 1 min and readding 700 Torr of H_2. With this procedure, adsorbed O atoms derived from the dissociation of NO on Pt were titrated to form water and TiO_2 was also further reduced by removing some lattice O atoms. After evacuation at 400°C again, 38 Torr of NO was redosed at room temperature and gave three absorptions with peak values at 1758, 1695, and 1472 cm^{-1} (Fig. 2a). Comparing Fig. 2a with Fig. 1d, we see suppression in the highest wavenumber band by about 30% while the shoulder declination is less than 10%. The band intensities for these and other conditions are summarized in Table I.

After evacuation of the pellet at 400°C for 30 min, it was reduced in H_2 at 500°C for 4 days. The H_2 gas was refreshed 10 times. After evacuation at 400°C, a quite different pellet background spectrum was formed (not shown). The absorption around 1200 cm^{-1} due to Ti–O lattice vibrations (*8*) diminishes significantly. With 18 Torr NO exposure, NO absorption bands are barely detectable (Fig. 2b). Increasing the NO pressure to 60 Torr (Fig. 2c), leads to only small changes in NO-derived bands, most noticeably at 1472 cm^{-1}. The increased intensity of the Ti–O lattice vibrations during the NO exposure (not shown) suggests that NO dissociation occurs on the Pt/TiO_2 surface and the derived O atoms oxidize the reduced TiO_2 surface. As a secondary result, we can see the oxidized NO species at the 1472 cm^{-1} band in Fig. 2c.

3.3. NO Adsorption on Pt/TiO_2 (400–200–400)

After reoxidation (i.e., the pellet went through the 400–200–400 treatment again). A very big absorption band appeared around 1200 cm^{-1} due to Ti–O lattice vibrations (not shown). Dosage of 18 Torr NO built up two bands and one shoulder at 1762, 1466, and 1701 cm^{-1} with intensities of 0.090, 0.005, and 0.036, respectively

TABLE 1

Infrared Spectra Data for NO Adsorption on Pt/TiO_2

Pretreatment[a]	P_{NO} (Torr)	Ratio of band intensity I_{open}/I_{close}	NO on Pt open sites wavenumber (intensity)	NO on Pt close-packed sites wavenumber (intensity)	Oxidized NO on TiO_2 wavenumber (intensity)
400–200–400	18	2.5	1762 (0.090)	1701 (0.036)	1466 (0.005)
	60	2.6	1765 (0.077)	1698 (0.029)	1472 (0.010)
(400)–200–400	18[b]	2.7	1732 (0.088)	1673 (0.033)	1453 (0.008)
400–400–400	42	1.6	1761 (0.052)	1698 (0.032)	1472 (0.008)
(400)–500–400[c]	38	1.2	1758 (0.037)	1695 (0.030)	1472 (0.008)
(400)–500–400[d]	18	—[e]	—[e]	—[e]	1472 (0.001)
	60	—[e]	—[e]	—[e]	1472 (0.008)

[a] See experimental section for detailed description of pretreatment notations.

[b] ^{15}NO chemisorption.

[c] H_2 Reduction overnight by refreshing H_2 gas 3 times.

[d] H_2 Reduction for 4 days with refreshing H_2 10 times.

[e] Barely detectable or hard to determine.

(Fig. 3a). That further exposure of 60 Torr NO enhanced only the 1466 cm^{-1} band indicates that at 18 Torr NO the Pt surface is almost saturated (Fig. 3b).

To check the reproducibility and to confirm that the 1762 and 1701 cm^{-1} bands are due to adsorbed NO while the 1466 band is accounted for as an oxidized NO species, the (400)–200–400 procedure was executed once more and followed by an 18 Torr ^{15}NO exposure. As indicated in Fig. 3c, there are three absorption bands, 1732, 1673, and 1453 cm^{-1} with peak intensities of 0.088, 0.033, and 0.008, respectively. This shows that the (400)–200–400 procedure is nicely reproducible. The isotope shifts for these three bands (compare Figs. 3a and c from left to right) are 30, 28, and 13 cm^{-1}, respectively. These values are in very good agreement with the theoretical values of 32, 30, and 14 cm^{-1} calculated assuming that the 1762 and 1701 cm^{-1} bands are due to adsorbed NO and the 1466 cm^{-1} band is for adsorbed NO_3^- species.

3.4. NO Uptake Studies

With one exception (Fig. 4e), the same sample, ca. 0.164 g Pt/TiO_2, was used for all NO uptake studies. These studies were performed in alphabetical order as shown in Fig. 4, i.e., Fig. 4a first and Fig. 4d last. The readsorption study (Fig. 4c), made after experiment 4b by pumping the system under a dynamic vacuum of 10^{-6} Torr at room temperature for 10 min, shows the amounts of weakly adsorbed NO on Pt/TiO_2. It is noteworthy that the four curves, Fig. 4a–d, are almost parallel to each other indicating that the Pt/TiO_2 surfaces are saturated with chemisorbed NO species above 15 Torr gaseous NO pressure. This is in agreement with the ir results which indicate that raising the NO pressure from 18 to 60 Torr has no significant influence on the peak heights of the bands for NO on Pt. By subtraction of curves (a), (b), and (d) from curve (c), the amounts of NO chemisorption on Pt/TiO_2 ((400)–200–400), Pt/TiO_2 ((400)–500–400), and the reoxidized Pt/TiO_2 (400–200–400) samples are estimated to be 18, 9, and 13 μmole/g, respectively. The partial recovery of NO uptake on the reoxidized Pt/TiO_2 (400–200–400) sample from the Pt/TiO_2 ((400)–500–400) sample strongly suggests that NO uptake also exhibits SMSI character. This is in agreement with the ir studies (Figs. 2 and 3). However, in these uptake studies, the NO uptake was not depressed to the extent shown in Fig. 2. One reason for the difference may be due to insufficient

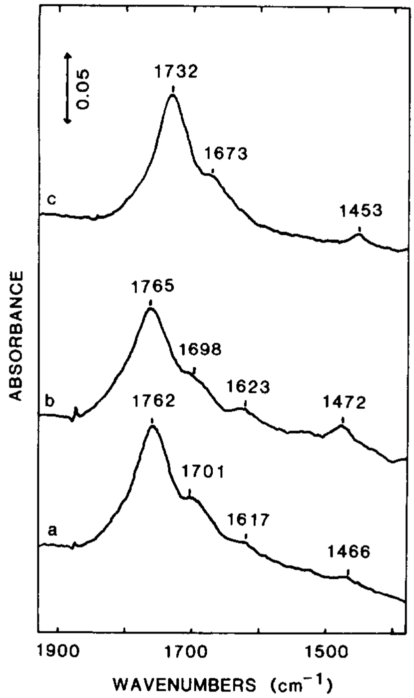

FIG. 3. Infrared spectra of NO adsorbed on Pt/TiO_2 (400–200–400): (a) 18 Torr NO exposure; (b) 60 Torr NO exposure; and (c) ir spectrum of 18 Torr NO adsorbed on Pt/TiO_2 ((400)–200–400).

reduction of the TiO_2 support, because for an SMSI Pt/TiO_2 sample (*7*) in which the TiO_2 had been strongly reduced in flowing H_2 at 875°C before platinization, the NO uptake is very small (Fig. 4e). Another reason is that ir would not detect dissociated NO uptake. The incomplete recovery of NO uptake may be due to sintering of Pt particles (compare curves d and a in Fig. 4). According to the uptake studies (H_2 and CO) by Baker *et al.* (*15*) reoxidation partially restores the chemisorption capacity of Pt supported on TiO_2. How NO dissociation correlates with the depression of NO uptake is not clear. However, an NO uptake study on Rh/TiO_2 indicates almost half the amount of the NO is dissociatively chemisorbed (*16*).

4. DISCUSSION

NO adsorption on well-defined Pt single crystal surfaces has been widely investigated by electron spectroscopic techniques. Comrie *et al.* (*13*) found a Pt(111) surface, probably containing a significant concentration of defects, was more active in inducing the thermal dissociation of NO when they compared the NO adsorption on both Pt(111) and Pt(110) surfaces at room temperature using LEED, AES, and TDS. The activation energy for NO desorption from the (111) face is about 27.5 kcal/mole. Work on the interaction of NO with a Pt(111) surface having a small concentration of defect sites by Campbell *et al.* (*17*) shows an activation energy for desorption from these defect sites of 33.1 kcal/mole and a preexponential factor $\vartheta_d \approx 10^{15.5}$ sec^{-1}. Both are very close to values obtained from Pt(110) studies. Gorte and Gland (*12*), using EELS, found two stretching frequencies at 1610 and 1760 cm^{-1} corresponding to NO adsorption in bridged and terminal sites, respectively, on Pt(110) above 170 K. They observed that the chemisorption of NO was predominantly molecular on the (110) face; however, a small amount of dissociation was detected with heating. For NO on Pt(111), two EELS bands at 1490 and 1710 cm^{-1} were also assigned as bridged and terminal bonded species by Gland and Sexton (*11*). Pirug *et al.* (*18*) used EELS to characterize NO on

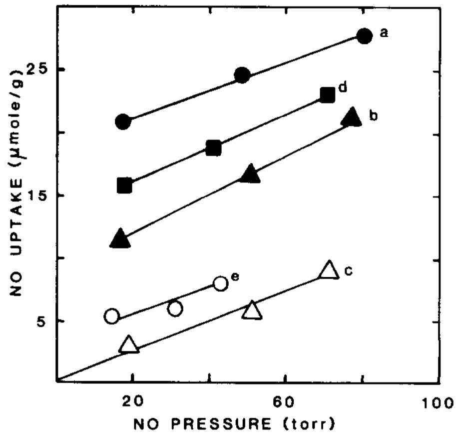

FIG. 4. NO uptake on Pt/TiO_2 (a) (400)–200–400; (b) (400)–500–400; (c) readsorption after pumping the NO gas in (b) at room temperature for 10 min; (d) 400–200–400; and (e) SMSI Pt/TiO_2.

Pt(100)-1 × 1 surface. An NO stretching frequency at 1645 cm^{-1} and two Pt–NO vibrations at 230 and 380 cm^{-1} were observed. They concluded absorbed NO has C_s symmetry and is bent with respect to the surface normal of Pt(100).

By comparison with the EELS results, we assign 1761 cm^{-1} mode in Fig. 1b as terminal NO on open Pt sites, for example, (110) and/or other high index faces, and the 1698 cm^{-1} band as terminal NO on Pt close-packed, (111) terraces with the understanding that the resolution of EELS is always about ± 10 cm^{-1}. NO adsorption on an annealed polycrystalline Pt surface studied by ir shows only one band at 1704 cm^{-1} at room temperature (*19*). This agrees with the above assignment because annealed Pt exhibits predominantly the (111) orientation. It should be noticed that the average platinum particle size in our catalyst was about 100 Å in diameter. Therefore, the above assignment based on single crystal work is reasonable.

A small shoulder at 1617 cm^{-1} in Fig. 3a is thought to be bridge-bonded NO on open Pt sites (*12*). The properties of this shoulder are difficult to determine because of the interference by the nearby broad bonds.

There is uncertainty whether the Pt particles supported on metal oxides exhibit (111) faces (*20*), because at low coverages of CO, (111) EELS results (*21, 22*) agree well with the observation from supported catalysts but high coverage results show some disagreement (*22*). In our experiment, Pt/TiO_2 (400–200–400) shows the most intense band at 1762 cm^{-1} and this has been assigned as terminal NO on open Pt sites. This might suggest that non-SMSI Pt particles on TiO_2 exhibit predominantly (110) faces and/or faces other than (111). This presumes that the extinction coefficient of NO is constant in the spectral region under consideration. Extensive reduction seems to lead to more terraces, Pt(111) faces, based on CO adsorption studies on Pt/TiO_2 (*6*) and electron microscope studies (*15, 23*). Further work for CO adsorption on Pt(110) and/or other high index planes would help confirm this point.

It is noteworthy that the peak height ratio of the two NO bands on Pt varies monotonically with the reduction temperature as shown in Table 1. Both from the peak height ratio and the absolute peak intensities, it seems that NO on open sites is significantly influenced by reduction while NO on terrace sites is less sensitive until both bands dramatically drop after long-term reduction at 500°C as shown in Fig. 2. To interpret the above variation, the following explanation is proposed.

Within the tight-binding approximation (TBA), the *d* occupancy changes in the order bulk < close-packed sites < open sites if $E_f < E_c$, the latter symbol denoting the center of gravity of the surface *d* band for close-packed sites (*24*). Within this framework, the center of gravity of the surface *d*-band for open sites, E_0, lies below E_c, as indicated schematically in Fig. 5. According to the Newns–Anderson approach (*25*), two localized bands are formed for each kind of surface site by interaction with the molecular state of NO, E_a (Fig. 5). The center of gravity of the antibonding band derived from the open surface states, E^*_{0a}, lies below that from close-packed surface

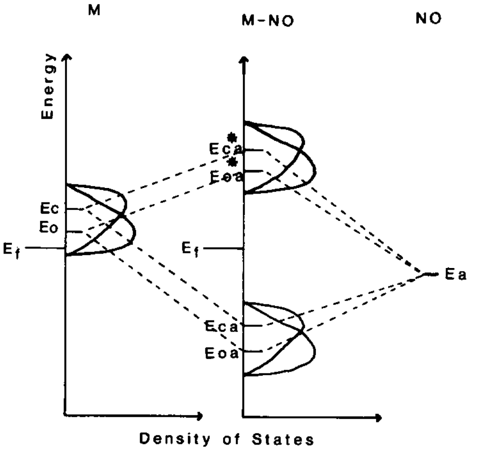

FIG. 5. Schematic representation of the energy levels for open and close-packed sites on metal before and after the interaction with NO.

states, E^*_{ca}. It has been suggested that the depression of CO and H_2 uptake can be attributed to electron transfer from the support to Pt particles. A local Pt–Ti bonding model (*26*) and a bulk charge transfer model (*7*) have been proposed and both probably participate. The electron transfer prefers the lower, open face, antibonding band centered at E^*_{0a}. As a consequence, NO on open sites is more significantly influenced by reduction. On the other hand, Baker *et al.* (*15*) using transmission electron microscopy concluded that the Pt morphology changes during the H_2 reduction process. The results are consistent with a model in which the total surface area of close-packed sites increases through the reduction and that of the open sites decreases. By itself this model cannot explain why the band intensity assigned to close-packed sites always decreases with the extent of H_2 reduction, since the surface area of these sites increases in this process. As a consequence, we propose that H_2 reduction induces electron transfer from support to Pt surface, preferentially to open sites. At the same time, the morphology is also modified in order to stabilize the accumulated charge arriving as a result of the transfer. Therefore, the loss of open site band intensity is partially due to morphology changes which decrease the number of open sites and to electron transfer which "poisons" the adsorption sites. The decay of the close-packed site band intensity with reduction indicates that the poisoning of close-packed sites due to electron transfer overrides the increased number of close-packed sites which appear as the result of morphology changes.

From the ir spectra and uptake studies, we find that the suppression of chemisorption on SMSI Pt/TiO_2 is not unique to H_2 and CO molecules but extends to NO as well. The formation of a bond between an occupied orbital in gas phase NO molecule and a surface Pt atom with unfilled valence *d*-orbital is expected to be necessary for the chemisorption of NO. Recently, Burch (*27*) has used an *electronic ligand effect* concept to interpret activity changes in metal alloy catalysts. To extend this concept, we suggest that the ligand effect is not only determined by the interaction between a metal atom and its neighbors, but also by long range charge transfer. In other words, we consider that the ligand effect can extend far beyond the nearest neighbors of a metal atom. This is analogous to the so-called *inductive effect* in organic chemistry. A non-SMSI Pt/TiO_2 particle is considered as a giant molecule in which Pt atoms have unfilled valence *d*-bands. For a surface Pt atom, the rest of the giant molecule can be thought of as its ligand. As long as the Pt valence *d*-orbital with the proper symmetry is unfilled, it can interact attractively with the occupied orbital of NO. If it is fully occupied, NO chemisorption on this Pt atom becomes possible through the promotion of electrons into other levels of this, or other, atoms. If the promotion energy is larger than (1) the stabilization energy due to the interaction between the empty *d*-orbital of Pt and occupied orbital of NO and (2) the backbonding stabilization, then chemisorption will be inhibited. In SMSI Pt/TiO_2, the ligand of the surface Pt atom is modified due to H_2 reduction. Not only is the *d*-orbital of the Pt atom filled due to long range electron transfer but other energy states within a certain energy range are also occupied and are not available for the promotion of electrons from the filled *d*-orbital of the Pt atom. Therefore, the bond formation between the NO molecule and the surface Pt atoms is unlikely. As a result, NO uptake is depressed.

5. CONCLUSION

In addition to H_2 and CO, nitric oxide uptake is also suppressed on SMSI Pt/TiO_2. To explain the interaction between Pt and a donor-type gas like NO, an extended electronic ligand effect concept is applied. Within this framework, depression of NO chemisorption is the result of filling Pt *d*-orbitals.

Two bands at 1762 and 1701 cm^{-1} have been assigned as terminal NO on open and close-packed sites, respectively. The significant loss of relative intensity of the 1762 cm^{-1} band with H_2 reduction is interpreted in terms of both a morphology change and a change of the density of states at surface Pt atoms.

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