JOURNAL OF CATALYSIS **172,** 3–12 (1997)
ARTICLE NO. CA971811

Reduction of NO by C_4 Hydrocarbons on Platinum in the Presence of Oxygen: Influence of Sulfur Dioxide

Wenhua Chen,* Hua Lu,* Claire-Marie Pradier,†,[1] Jan Paul,* and Anders Flodström*

**Materials Physics, Royal Institute of Technology/KTH, 100 44 Stockholm, Sweden; and †Physico-Chimie des Surfaces, Ecole Nationale Supérieure de Chimie de Paris, 11 Rue P.et M. Curie, 75005 Paris, France*

Received November 4, 1994; revised June 9, 1997; accepted June 30, 1997

The reduction of NO, in the presence of i-C_4H_{10} or i-C_4H_8 and O_2, catalyzed by a platinum foil, was studied in order to understand better the catalytic activity of platinum metal, free of any support or dispersion effects. The reaction products were analyzed by mass spectrometry, and the surface was characterized by X-ray photoelectron spectroscopy at different stages of the reaction. A correlation between the catalytic activity for NO conversion and the presence of adsorbed intermediates is demonstrated. The role of oxygen is interpreted as twofold: formation of active intermediates and deactivation of the surface. The effect of traces of sulfur dioxide in the reacting phase on the reduction of NO by isobutene was investigated. The influence of SO_2 is very much dependent upon its initial concentration in the gas phase. Low concentrations ($<$15 ppm) promote the reduction of NO, whereas higher levels poison the reaction by a surface site blocking effect. © 1997 Academic Press

INTRODUCTION

The reduction of NO over Group VIII metals has been extensively studied in relation to the control of pollution from exhaust gases. Supported metals are usually investigated and it has been made clear that the support and the metallic particle size do influence the catalytic activity (1). The use of hydrocarbons as reductants, instead of NH_3 or H_2, is a subject of interest since it avoids transportation and equipment corrosion problems (2–5). Ethylene and propylene are currently the most studied reactants for the reduction of NO (6, 7), and the reduction of NO in the presence of oxygen has been intensively reported using Cu/ZSM-5 as a lean NO_x catalyst. The catalytic sequence in the reaction of NO, hydrocarbon (HC), and O_2 is complicated. It involves several steps which are consecutive or competitive. The initial oxidation of NO to NO_2 is a possible preliminary step; the partially oxidized hydrocarbon as a reaction intermediate on copper-based catalysts has also been suggested, but none of these hypotheses has been made clear so far (8–10). Cu/ZSM-5 was proved to be capable of reducing NO under lean conditions but not stable enough to be a long-term platinum substitute. The use of precious metals has regained attention (11); however, little is known about the reactivity of hydrocarbons higher than C_3 on Pt in the presence of NO and oxygen. The better durability of precious metal catalysts and the actual presence of these higher alkanes and alkenes in diesel exhaust gas has motivated our choice of platinum as the catalyst to be studied and of C_4 hydrocarbons as the reductants. The progress of this reaction is known to require the presence of oxygen, the role of which, at various stages of the reaction, is still questioned.

We believe that a better understanding of the surface chemical processes in HC reduction of NO on Pt is a way to determine the optimum conditions for operating a Pt-based catalyst in the NO reduction mode. In the present experiments, an unsupported pure platinum sample was used as the catalyst to avoid the transport limitations and support effects common to dispersed catalysts.

In the first part of this work, two C_4 hydrocarbons, isobutane and isobutene, were tested as reducing agents in order to make the influence of unsaturation upon reactivity clear.

In the second part, we investigated the effect of low concentrations of sulfur dioxide in the gas mixture upon the catalytic activity of Pt for NO reduction. In the latter study, the reductant was isobutene. This is of practical importance because SO_2 is present as an impurity in real combustion gases and is generally considered to be responsible for deactivation of the catalyst (12, 13).

In both reactions, namely, those involving isobutane and isobutene, the influence of the oxygen partial pressure was investigated, and the catalytic activity determined from reaction experiments was correlated with the characterization of the Pt surface obtained by X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

The catalyst used was a planar polycrystalline, 5N purity, platinum foil, 6.25 cm^2 in area; it was mechanically polished and rinsed in alcohol before being cleaned *in situ*.

---

[1] To whom correspondence should be addressed. Fax: 33 1 46 34 07 53.

0021-9517/97 $25.00

The Pt sample was reduced in hydrogen at a temperature of 1200 K for 2 h before each experiment. The cleanness of the platinum surface after the hydrogen reduction was checked by Auger electron spectroscopy (AES). The peak to peak amplitudes of the Pt_{MNN} (237 eV), C_{KVV} (274 eV), and O_{KVV} (506 eV) signals indicated very little carbon and an oxygen coverage of less than one monolayer.

A 18-dm^3 quartz tube was used as a reactor. The platinum foil was placed inside the quartz reactor, which was heated by an external furnace. In order to measure the reaction temperature, a chromel–alumel thermocouple was placed in contact with the walls of the reactor. A small constant leak from the reactor to a quadrupole mass spectrometer (Balzers, QMA 125) was maintained to enable the gas composition to be analyzed during the reaction. The reactor chamber was connected to a UHV chamber equipped with conventional surface analysis tools. The sample was transferred between the two chambers under vacuum.

The catalysis experiments were performed in a static mode in the reactor; this allowed investigation of the catalytic surface to be made at various stages of the reaction, at low or high NO conversion rate corresponding to various concentrations of products of the reaction. The purpose of this work was to observe and characterize various surface states throughout a catalytic process rather than to apply conditions relevant to sustained catalysis.

At different stages in the reactions, the Pt sample was cooled, the reaction gases were pumped away, and the sample was then transferred under UHV to the surface analysis system. XPS was performed on a VG spectrometer also equipped with an AES facility. In the XPS mode, Mg$K\alpha$ (1253.6 eV) radiation was used as the excitation source and the electron kinetic energies were analyzed by a CLAM 2 hemispherical energy analyzer utilizing a pass energy of 20 eV. A small gold foil was attached to the platinum sample to provide an internal reference for the binding energies. Binding energies were corrected for charging effects by taking the BE of Au $4f_{7/2}$ as 84 eV. The accuracy of the binding energy values was better than 0.3 eV. For AES measurements, an electron gun was operated at an electron energy of 3 keV, and the beam current was maintained at 200 nA. Direct $n(\mathrm{E}) = f(\mathrm{E})$ spectra were taken and computer transformed into derivative curves.

The surface characterization and kinetics data were correlated with each other in order to understand better the various steps of the reactions investigated.

RESULTS

1. *Kinetics*

1.1. Reduction of NO in the presence of i-C_4H_{10} and O_2. Figure 1 shows the nitric oxide and isobutane conversion traces for a reaction run at 740 K with the following partial pressures: $P_{O_2} = 1.5$ Torr, $P_{NO} = 1.2$ Torr, $P_{\text{i-}C_4H_{10}} = 0.3$ Torr. These pressures correspond to slightly oxidizing conditions, the stoichiometric number, S, used as a redox characteristic for the gas mixture, being defined as in Ref. (14): $S = (2P_{O_2} + P_{NO})/13P_{\text{i-}C_4H_{10}} = 1.08$. For $S < 1$, $S = 1$, $S > 1$, the gas mixture is reducing, stoichiometric, or oxidizing, respectively. Three stages of the reaction are observed once the temperature has reached the desired value. In stage 1, O_2 and i-C_4H_{10} are rapidly consumed, yielding H_2O and CO_2. In about 30 min, 80% of the initial amount of oxygen is consumed without any decrease of NO. In stage 2, NO is converted at a constant rate equal to 4 molecules Pt $\text{atom}^{-1}\ \text{s}^{-1}$. At the same time, oxygen and i-C_4H_{10} still decrease. The main products resulting from the conversion of NO and i-C_4H_{10} are N_2, CO_2, CO, and H_2O. The third stage of the reaction is characterized by low amounts of O_2 and i-C_4H_{10} left in the gas phase and a decreasing rate of NO conversion.

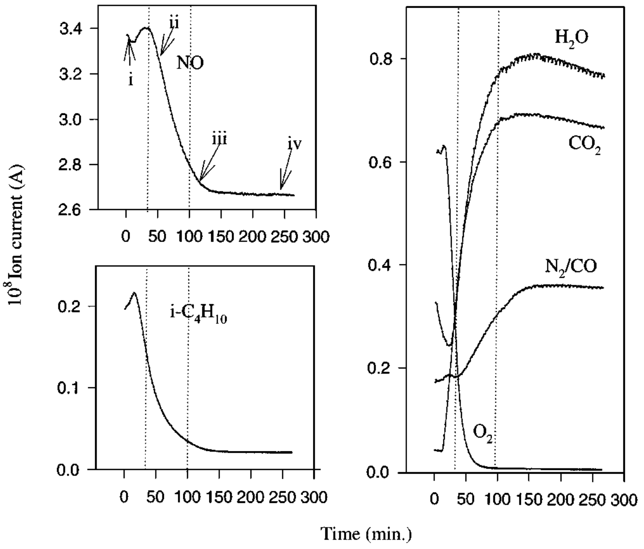

FIG. 1. Time course of the reaction run at 743 K, $P_{NO} = 1.2$ Torr, $P_{O_2} = 1.5$ Torr, and $P_{C_4H_{10}} = 0.3$ Torr.

1.2. Reduction of NO in the presence of i-C_4H_8 and O_2. The conversion of NO was investigated using the same experimental procedure and the same catalyst as described in Section 1.1. Slightly reducing conditions were chosen after reactions had been tested under various pressures of reactants. We adopted the conditions $P_{O_2} =$ 1.5 Torr, $P_{NO} = 1.2$ Torr, $P_{\text{i-}C_4H_8} = 0.4$ Torr, corresponding to $S = (2P_{O_2} + P_{NO})/12P_{\text{i-}C_4H_8} = 0.90$, and $T = 693$ K, because they led to a reasonable rate of NO conversion; we call these "standard" conditions in the rest of the text.

Figure 2, shows the time course of the reaction; the differences in the process of NO conversion in the presence of i-C_4H_8 compared to i-C_4H_{10} (Fig. 1) are remarkable. A monotonic decrease in the amount of the three reactants is observed as soon as the reaction temperature is reached.

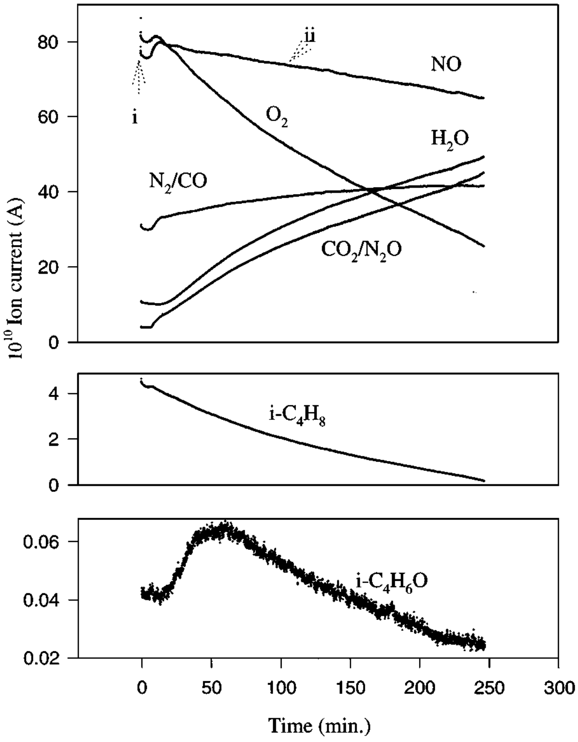

FIG. 2. Time course of the reaction run at 693 K, $P_{NO} = 1.2$ Torr, $P_{O_2} = 1.5$ Torr and $P_{C_4H_8} = 0.4$ Torr. i-C_4H_6O signifies 2-methyl-2-propenal (methacrolein).

Oxygen is the most rapidly consumed reactant. Note the extent to which this is different from the reaction with isobutane conducted under similar conditions. In the latter case, the conversion of NO started only after a preliminary reaction of oxygen with the hydrocarbon. In the present case, the rate of NO conversion is constant, equal to 2 molecules (Pt atom)$^{-1}$ s^{-1}, until isobutene is totally consumed, after 5 h under our conditions. It then decreases but does not halt as long as oxygen and NO are still present in the gas phase. The main products resulting from the conversion of NO and i-C_4H_8 are N_2, CO_2, CO, and H_2O. Mass peaks at, respectively, 67 and 70 amu, detected at certain stages, were unambiguously assigned to $CH_2{=}CCH_3CN$ (2-methyl-2-propenenitrile) and $CH_2{=}CCH_3CHO$ (2-methyl-2-propenal, i.e., methacrolein), their fragment peaks had been checked. The formation of N_2O is negligible and the production of NO_2 is small as long as isobutene is still present in the reacting gas phase. An interesting feature is the initial increase of methacrolein, denoted as i-C_4H_6O, resulting from a mild oxidation of isobutene, which is converted again at a later stage of the reaction.

The reduction of NO with isobutene was also tested at various temperatures from 563 to 773 K. Both the rate of formation of $CH_2{=}CCH_3CHO$ at the beginning of the reaction and the rate of NO conversion were found to be maximal at 693 K.

1.3. Influence of P_{O_2} upon the conversion of NO. When the reducing agent is i-C_4H_{10}, the rate of NO conversion goes through a maximum at $P_{O_2} = 1.5$ Torr ($S = 1.08$), as shown in Fig. 3. All the reactions were run at 740 K. The rates of NO and HC conversion decrease when the O_2 pressure decreases from 1.5 to 0.3 Torr. Note that, in the absence of oxygen, the conversion does occur; it starts at a low rate and then reaches a stationary value roughly 50% lower than at the optimal P_{O_2} of 1.5 Torr. At a higher O_2 pressure (3 Torr), the conversion of NO is negligible.

When the reducing agent is i-C_4H_8, there is no conversion of NO over Pt without oxygen.

At 693 K, the conversion of NO starts when the O_2 partial pressure (P_{O_2}) is higher than 0.7 Torr ($P_{NO} = 1.2$ Torr, $P_{i\text{-}C_4H_8} = 0.4$ Torr). The rate further increases with P_{O_2}, the rate curves having the same shapes as those in Fig. 2. A reaction was also performed with $P_{O_2} = 3$ Torr; the rate was only slightly lower than that at $P_{O_2} = 1.5$ Torr, but NO_2 was the main product of NO conversion.

1.4. Influence of SO_2 in the reacting gas phase. The influence of sulfur dioxide in the conversion of NO by i-C_4H_8 at 693 K was investigated. Reactions were performed with the same partial pressures of NO, O_2, and i-C_4H_8 as in Section 1.2 and with the partial pressure of SO_2 increasing from 1.5×10^{-6} Torr (0.48 ppm) to 5×10^{-5} Torr (16 ppm). Figure 4 shows the dependence of the rate of NO reduction and of the onset of $CH_2{=}C(CH_3)CHO$ (i-C_4H_6O) formation upon the initial SO_2 partial pressure. In the very low pressure range, sulfur dioxide promotes both the conversion of NO and the initial formation of methacrolein. At higher levels of SO_2, still corresponding to trace amounts in the gas phase, the selective oxidation of isobutene is still slightly promoted but the NO conversion starts to be poisoned. Similarities and differences in the behavior of these two reactions will be commented on in the discussion.

Promotion by low trace amounts of sulfur dioxide was reproducible without accumulation of sulfur on the surface. No poisoning of the surface was observed after a series of reactions performed in the presence of low traces of SO_2.

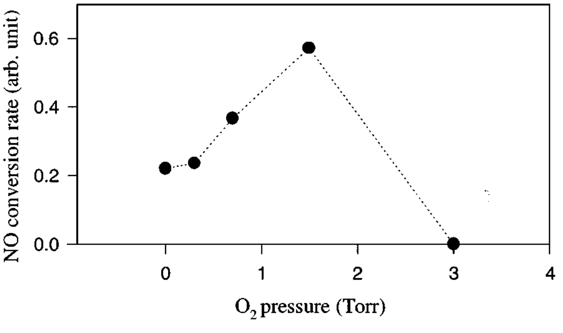

FIG. 3. Oxygen pressure dependence of NO conversion, $P_{NO} = 1.2$ Torr, $P_{C_4H_{10}} = 0.3$ Torr, $T = 740$ K.

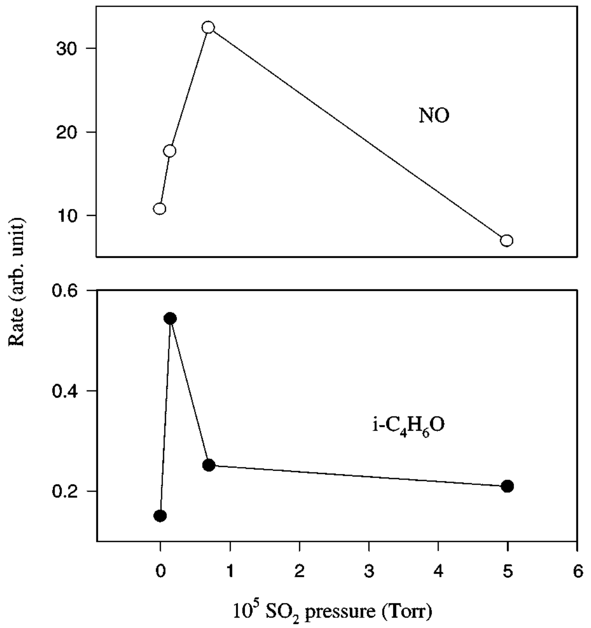

FIG. 4. Rate of NO reduction (open circles) and $CH_2{=}C(CH_3)CHO$ formation (filled circles) as a function of SO_2 partial pressure; same conditions as in Fig. 2.

This result is of great importance for comparison with the flow mode or with real catalytic conditions. In the latter case, the catalyst is continuously exposed to new amounts of NO, hydrocarbon, O_2, and low concentrations of SO_2. However, poisoning by high trace amounts was found to be irreversible under reaction conditions, and high-temperature hydrogen treatment was not sufficient to recover the initial platinum activity.

2. Characterization of the Catalytic Surface

The catalytic surface was characterized by XPS after gas evacuation and sample transfer to the UHV chamber, following different times of reaction.

2.1. i-C_4H_{10} as reducing agent. When i-C_4H_{10} is the reducing agent, the active surface of platinum exhibits the O 1*s* and C 1*s* spectra shown in Fig. 5 (i) in the initial stage, (ii) in the second stage (maximum NO conversion rate), (iii) in the third stage (low NO conversion rate), and (iv) when the conversion of NO is stopped.

Fractions of converted NO and i-C_4H_{10} are given below:

—at (i), reaction not started,
—at (ii), 4% of NO, 42% of i-C_4H_{10} converted,
—at (iii), 20% of NO, 60% of i-C_4H_{10} converted, and
—at (iv), 22% of NO, 62% of i-C_4H_{10} converted.

(i) After the "cleaning" treatment under hydrogen at 1200 K, a small and broad O 1*s* peak is detected at 532.6 eV. It is likely to originate from both OH groups and CO adsorbed species left after hydrogen treatment (15). Very little carbon is detected at this stage.

(ii) At the most active stage of the reaction, a huge increase in the oxygen signal is observed. The O 1*s* line can be fitted to two contributions, one at 532.0 eV and a second

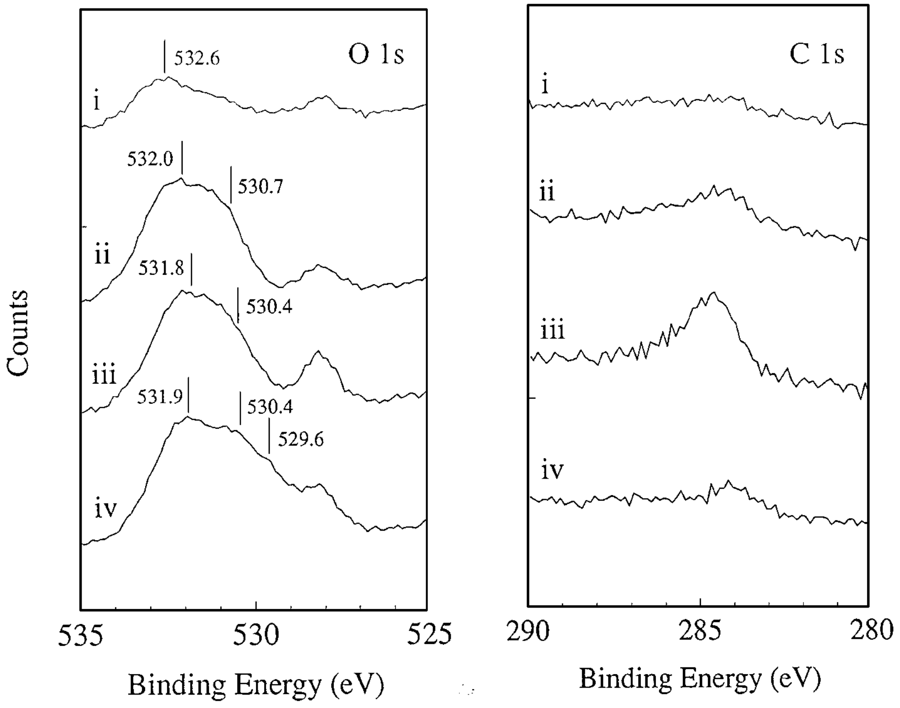

FIG. 5. X-ray photoelectron spectra of O 1*s* and C 1*s* core levels from Pt surface at different stages of the reaction with i-C_4H_{10} (same conditions as in Fig. 1) (i) initial stage after "cleaning"; (ii) maximum rate of NO reduction; (iii) low rate of NO reduction; (iv) reduction of NO stopped.

at 530.7 eV binding energy. A weak C 1*s* peak is detected at this stage.

(iii) At the following, less active, stage of the reaction, the O 1*s* signal is sharper and less intense than at the second stage. The signal results from the contribution of two peaks at 530.4 and 531.8 eV, respectively. A simultaneous increase of the C 1*s* peak is observed at 284.8 eV.

(iv) At the final, inactive, stage of the reaction, the O 1*s* signal is broader and more intense than at any other stage. It is well fitted with three peaks, two at binding energies similar to those in the third stage spectrum and an additional one at 529.6 eV. Note that the 530.4 eV BE contribution is greater than at the third stage of the reaction. The corresponding C 1*s* signal is weak.

The N 1*s* signal was checked in all four stages. No peak could be detected, indicating that the identified surface species do not contain nitrogen atoms.

A weak peak was constantly observed at 528 eV due to an uncontrolled contamination by antimony. The coverage of antimony was evaluated from the Sb Auger signal at 454 eV compared to the platinum Auger peak at 237 eV in the derivative mode; it was below 0.2 monolayer and was found not to influence the mechanism of the reaction.

Note also that no shift or change in shape was detected for the Pt 4*f* peak during the reaction (spectra not shown). Only a single inelastic Pt $4f_{7/2}/4f_{5/2}$ doublet was observed at 70.9 and 74.2 eV. Pt(IV) oxide has a chemical shift of 2.9 eV toward a higher binding energy, whereas a chemical shift of 1.5 eV has been reported for Pt(II) oxide (16, 17). This proved that the platinum surface was in the metallic state throughout the reaction.

2.2. i-C_4H_8 as the reducing agent. When i-C_4H_8 was the reducing agent, XP spectra from the Pt surface were taken at three stages of the reaction, (i) before gas introduction, (ii) after reaction for 1.5 h (high NO conversion rate), and (iii) after reaction for 5 h (low rate with no i-C_4H_8 left in the gas phase). Fractions of converted NO and i-C_4H_8 are given below:

—at (i), reaction not started,
—at (ii), 7% of NO, 48% of i-C_4H_{10} converted, and
—at (iii), 25% of NO, 100% of i-C_4H_{10} converted.

Figure 6 shows the O 1*s* and C 1*s* regions of the XP spectrum.

The shapes and intensities of the O 1*s* line are very dependent upon the stages in the reaction. A weak and broad oxygen peak is present at the initial state of the surface. The most active stage of the reaction is characterized by a sharp O 1*s* line with a shoulder at lower binding energy. A curve fitting gives two contributions at 532.2 and 531.0 eV, respectively. After 5 h, the O 1*s* line is much less intense; it is also well fitted with two peaks, at binding energies very similar to those in the most active stage, at 532.5 and 531 eV.

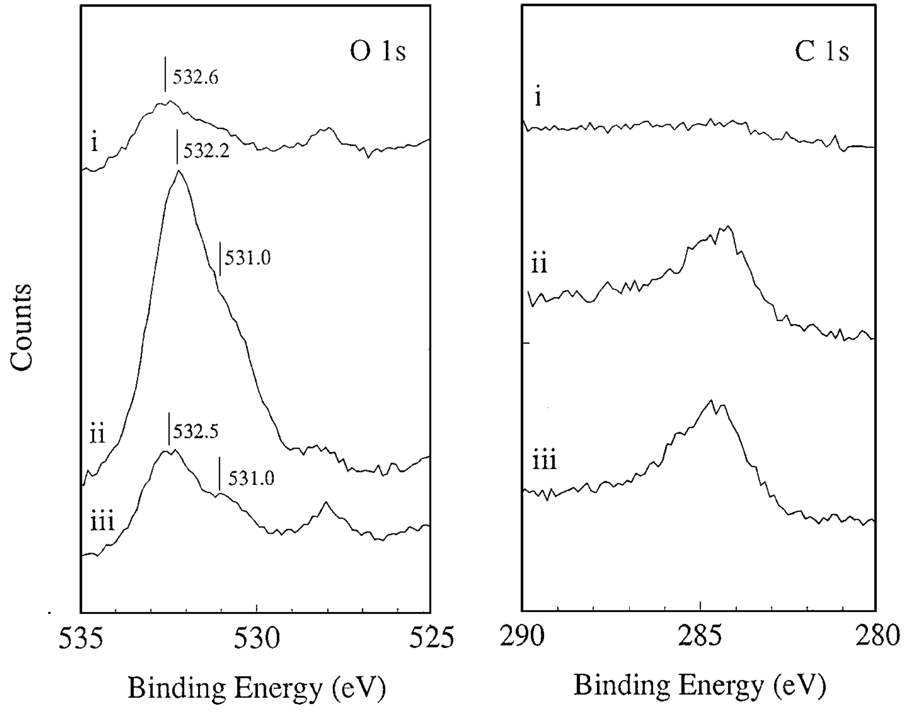

FIG. 6. XP spectra of O 1*s* and C 1*s* core levels from Pt surface at different stages of the reaction with i-C_4H_8 (same conditions as in Fig. 2) (i) initial stage after “cleaning”; (ii) maximum rate of NO reduction; (iii) slow reduction of NO.

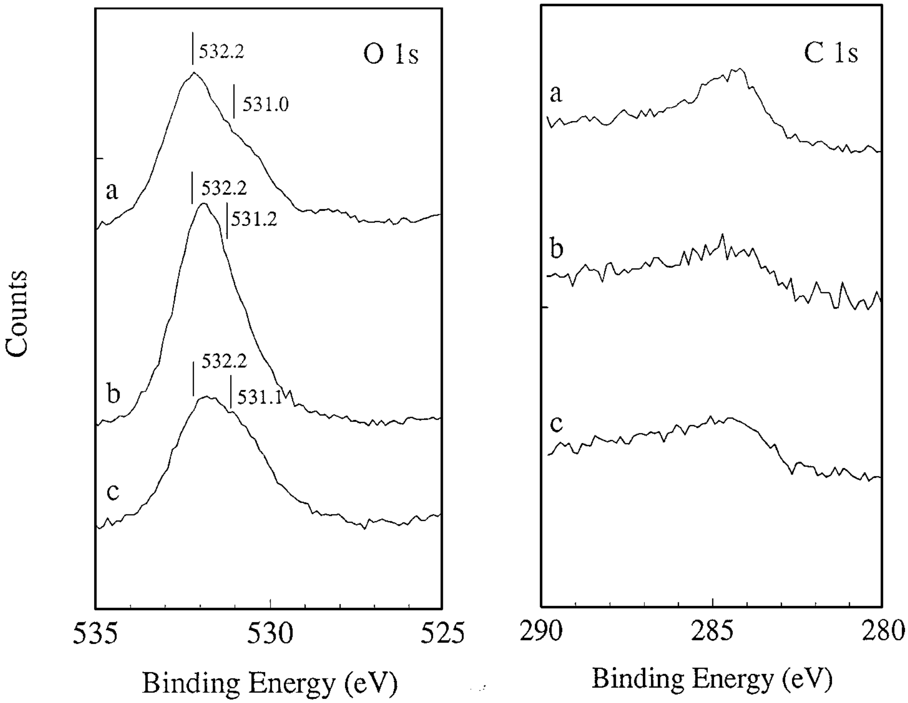

FIG. 7. XP spectra of O 1*s* and C 1*s* core levels from Pt surface when the rate of the reduction of NO run with i-C_4H_8 is maximum (same conditions as in Fig. 2), with different pressures of SO_2, (a) without SO_2; (b) $P_{SO_2} = 1.5 \times 10^{-6}$ Torr; (c) $P_{SO_2} = 5 \times 10^{-5}$ Torr.

The C 1*s* line is broad and has roughly the same intensity at all stages of the reaction.

A weak N 1*s* signal was detected at all stages of the reaction. No significant changes in its shape or intensity were noticed (spectra not shown).

For an easier comparison of the active surface state in the above two types of reaction, the O 1*s* peak positions are summarized in Table 1.

The most active surface was also characterized by Auger and XP spectroscopy when the i-C_4H_8 + NO + O_2 reaction was run in the presence of sulfur dioxide. The O 1*s* and C 1*s* regions of XP spectra, corresponding to a reaction run (a) without sulfur dioxide, (b) with a low (0.48 ppm), and (c) with a high (16 ppm or 5×10^{-5} Torr) initial concentration of SO_2, are presented in Fig. 7. Auger spectra corresponding to reactions run with low and high levels of SO_2, respectively, are shown in Fig. 8.

A remarkable feature in Fig. 7 is the change in the O 1*s* profile when the amount of sulfur dioxide varies. Compared to a reaction run in the absence of sulfur dioxide, the O 1*s* signal at low SO_2 concentrations is sharper and more intense. The result of a peak fitting is given in Table 2. At a high SO_2 concentration, the O 1*s* signal is smaller and

TABLE 1

Binding Energy of the O 1*s* Contributions from Pt Surface at Different Stages of the Reactions NO + i-C_4H_{10} + O_2 and NO + i-C_4H_8 + O_2

	O 1*s* binding energy (eV)				
	In the presence of i-C_4H_{10}			In the presence of i-C_4H_8	
Initial stage			532.6		532.6
Most active		530.7	532.0	531.0	532.2
Less active		530.4	532.2	531.0	532.5
Poisoned	529.6	530.4	532.1		

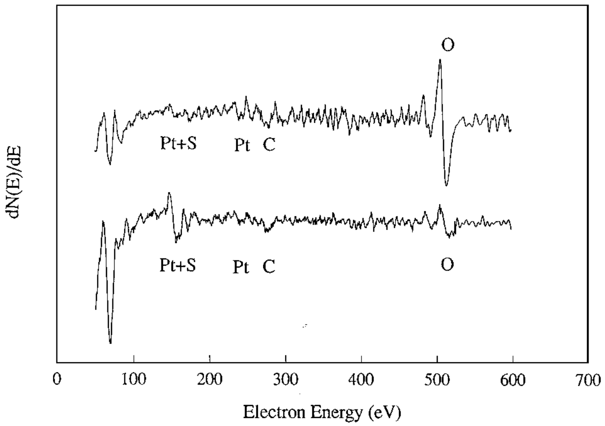

FIG. 8. Auger electron spectra from Pt surface corresponding to the NO + i-C_4H_8 + O_2 reactions run with $P_{SO_2} = 1.5 \times 10^{-6}$ Torr (top spectrum), $P_{SO_2} = 5 \times 10^{-5}$ Torr (bottom spectrum).

TABLE 2

Binding Energy of the O 1*s* Contributions and Relative Activities of the Pt Surface in the $NO + i\text{-}C_4H_8 + O_2$ Reaction with Different Amounts of SO_2

P_{SO_2} (Torr)	Relative activity	O 1*s* binding energy (eV)	
0	a_0	531.0	532.2
1.5×10^{-6}	$1.8a_0$	531.2	532.2
5.0×10^{-6}	$0.7a_0$	531.1	532.2

broader than in the previous case. Let us note that, whether in the absence or in the presence of sulfur dioxide, two peaks were found to contribute to the oxygen profile at very similar binding energies. Only their respective intensities vary. The XPS sulfur peak was, in all cases, very weak (spectra not shown).

It should be mentioned that the binding energies and the shapes of the Pt 4*f* core levels were not found to be changed at any stages of the reaction either in the absence or in the presence of SO_2. Table 2 gives the relative catalytic activities and BE values of the O 1*s* contributions corresponding to different pressures of SO_2.

DISCUSSION

A comparison of the $NO + i\text{-}C_4H_{10} + O_2$ and $NO + i\text{-}C_4H_8 + O_2$ reactions over platinum is made in the following section. Large differences were found in the time courses of these reaction processes.

In the presence of the saturated hydrocarbon isobutane, the conversion of NO is preceded by an induction period corresponding to the almost total consumption of oxygen. Before the reaction starts, the surface is partially covered with OH groups or water as indicated by a residual broad O 1*s* peak at 532.6 eV and no C 1*s* signal (Fig. 5). Platinum is not altered by a reaction with oxygen, suggesting that this initiation stage is the consequence of a competition between NO and O_2 as oxidants for isobutane rather than an activation step of the metal surface. NO starts to be consumed by reaction with the hydrocarbon or a derived product once the oxygen level has become very low.

In the case of the unsaturated hydrocarbon isobutene, no preliminary period is observed. A possible explanation is that the unsaturated hydrocarbon, more active than isobutane, first undergoes an oxidation; it forms an unsaturated aldehyde, detected in the gas phase, a very reactive intermediate which immediately reduces NO. As a matter of fact, both the catalytic experiments and the XPS data strongly suggest that the activity of platinum in the reduction of NO is related to its ability to selectively oxidize isobutene into methacrolein. On the one hand, the highest rate of NO reduction was obtained when Pt had the highest initial selectivity to partial oxidation of isobutene. On the other hand, the main contribution of the sharp O 1*s* peak to the O 1*s* XP spectrum, at 532.2 eV, observed at the most active stage of the reaction (Fig. 5, spectra (ii)), can be ascribed to active surface species resulting from the interaction between isobutene and oxygen. Note that the amount of methacrolein remains small throughout the reaction because it immediately reacts with NO.

The smallest contribution, at 531 eV, cannot be unambiguously identified; it may originate from CO-containing components or from OH groups (18). These surface species are not clearly correlated to the catalytic activity of the surface. The role of oxygen is likely to be twofold, to "clean" the surface from carbon poisoning and to form reactive intermediates. This also explains why no conversion of NO was observed in the absence of oxygen when isobutene was the reductant.

Whether isobutane or isobutene is used as the reductant, the most active stage of the reaction is characterized by two O 1*s* contributions close to 531 and 532 eV. The former was attributed to inactive, C- and O-containing species which deactivate the surface; it may also originate from molecular oxygen (19). We ascribe the latter to active intermediates which also contain carbon and oxygen atoms and which actually take part in the reaction. These active intermediates may be alcoholic or aldehydic fragments. None of the identified surface intermediates contain −NCO fragments, the formation of which would have been expected on platinum surfaces (20). At these high temperatures, −NCO is likely to dissociate or react rapidly with NO to N_2 and CO_2 (21).

It is also probable that NO dissociates on platinum, and N_2 desorbs, but this is not the main reaction pathway, since the reaction, measured in the absence of hydrocarbon, was slower by a factor of 10 than in the presence of isobutane. The formation of a reactive intermediate from the interaction of a hydrocarbon and oxygen has already been observed by Bennett *et al.* on copper (9). These authors also exclude mechanisms that involve NO decomposition.

Note that the maximum rates of NO conversion are of the same order of magnitude with both hydrocarbons studied. We have no clear interpretation of this phenomenon. In our opinion, it indicates that the presence of C=C unsaturation plays a role in the initial stage of the reaction, i.e., in the consumption of oxygen, but not in the rate-determining step of the reaction, which is likely to be the reaction of NO with a surface intermediate.

The surface state at the later stages of the reactions, corresponding to a decrease of activity, depends upon the nature of the reductant, as follows.

With isobutane, at the third stage of the reaction (Fig. 5, spectra (iii)), the significant change in the XP spectra is the increase in the C 1*s* line and the small shift of the O 1*s*. Carbon deposits on the surface, together with a low residual pressure of oxygen, account for a progressive decrease of the rate of conversion of NO. At this stage, we do not exclude the existence of OH groups on the surface; they would contribute to the oxygen line at around 532 eV (22).

Finally, at the last stage of the reaction, in addition to the two identified contributions, a third O 1*s* peak grows at 529.6 eV characteristic of chemisorbed oxygen on the surface (18, 19), which obviously has no promoting effect on the reaction. At this stage, hydrocarbon and O_2 have been almost totally consumed.

With isobutene, the significant decrease in the peak at 532.2 eV (Fig. 6, spectrum (iii), left side) can be correlated with the diminution in the catalytic activity observed after 5 h, when no hydrocarbon is left in the gas phase. It is worth noting that, unlike the same reaction performed in the presence of isobutane, the present reaction, run with oxygen present in the gas phase throughout the conversion of NO, does not halt because of an increase in carbon or oxygen deposits on the surface. After a long period, more than 10 h, NO is still converted but via another mechanism involving only NO and oxygen and leading to NO_2 as the main product. We ascribe the weak nitrogen peak, present throughout the reaction, to adsorbed NO at a low coverage.

We have shown that a reactant formed by selective oxidation of isobutene is mainly involved in the reduction of NO. Moreover, the reduction of NO in the absence of O_2 cannot proceed even at 693 K, which is the optimum temperature for the reaction in the presence of oxygen. This excludes the reaction pathway of NO decomposition on Pt and direct reduction of NO by i-C_4H_8 and leads to the conclusion that an unsaturated aldehyde, known to be very reactive, may be a better reducing agent for NO reduction than hydrocarbons. The addition of one oxygen atom to the reductant was shown by Iwamoto to greatly promote the nitric oxide reduction (23). Recent results on Cu/ZSM-5 by Montreuil and Shelef (10) also make clear that partially oxygenated reductants for NO are more active than hydrocarbons on Cu/ZSM-5 when the gas composition approaches the stoichiometry, as in our case. Some further experiments will be carried out utilizing oxygen-containing compounds as reducing agents for NO and varying the gas composition.

Another mechanism for the reduction of NO at 573 K in the presence of C_3H_6 on Pt/Al_2O_3, involving reduction of Pt–O patches followed by NO dissociation, has been proposed by Ansell *et al.* (11). Such a mechanism cannot account for the reactivity of platinum at a higher temperatures, when platinum would be immediately recovered with oxygen and reactions must take place on an oxygen-covered platinum surface.

The optimum temperatures of 740 and 693 K for the reduction of NO in the presence of isobutane and isobutene, respectively, are high compared to those reported on Pt- or Pt–Rh-supported catalysts (24, 25) for the reduction of NO by hydrogen. They are also higher than the temperature reported by Burch *et al.* (26), who showed that propene is a better reductant than H_2 at 550–650 K, the optimum temperature varying with the precursor of the supported platinum catalyst. On pure, nonsupported platinum, little is known about the reaction of NO in the presence of hydrocarbon. However, the probability for alkane and alkene activation to occur is very low at temperatures below 600 K (27).

Reduction of NO by Isobutene in the Presence of SO_2

The inhibiting effect of sulfur on NO_x reduction on noble metal catalysts as well as on copper-containing catalysts has already been documented (28–30). Usually, both the maximum activity for NO conversion and the low-temperature performance of catalysts deteriorated in the presence of SO_2. In contrast, our experimental results obtained under slightly reducing conditions show that low concentrations of SO_2 in the gas phase accelerate the reduction of NO. The poisoning of the reduction of NO by i-C_4H_8 on Pt was observed only when the concentration of SO_2 was higher than 15 ppm. This finding is of practical importance since the removal of NO emission might be achieved by the control of SO_2 to a low level. This is in good agreement with the results of Zhang *et al.*, who recently found that SO_2 addition improved the activity of Pt/BSA (boria–silica–alumina) catalyst for the reduction of NO by C_3H_6 in the presence of O_2 (5). The promoting effect of sulfur dioxide can be related to similar effects observed in reforming catalysis and recently reviewed by Rostrup-Nielsen (31). Sulfur was shown to increase the selectivity of reforming on platinum (32); the reason is that hydrogenolysis, which is the undesired pathway, is a more demanding reaction than isomerization or hydrogenation. Ensemble control is also likely to play a determining role in our present work; the selective oxidation of isobutene, which is obviously a less demanding reaction than cracking or hydrogenolysis of the hydrocarbon, will be favored in the presence of a fraction of a monolayer of sulfur on the surface. An optimum sulfur level of the order of 1000 ppm in the reacting gas phase was demonstrated by Hayes *et al.* for reforming reactions (33). Such a high level is not surprising in view of the chemisorption equilibrium $H_2(g) + S_{ads} \rightleftharpoons H_2S(g)$. The pressure ratio $P(H_2S)/P(H_2)$ corresponding to a coverage of 0.9 was calculated to be equal to 2×10^{-7} at 740 K for platinum in a pure H_2, H_2S mixture (34). However, in the presence of hydrocarbons, sulfur adsorption isotherms are known to be displaced toward $P(H_2S)/P(H_2)$ values higher by several orders of magnitude (35).

We do not exclude the possible dissociation of SO_2 into sulfur and oxygen, enhanced by slightly reducing reaction conditions. Sulfur would, at low coverage, induce an electronic effect promoting the activation of isobutene on platinum and in turn favor the formation of aldehydic intermediates.

In the present experiments, the sulfur coverage was estimated by monitoring the sulfur Auger transition at 151 eV.

A platinum peak overlaps with the sulfur peak, so it is convenient to quantify sulfur on Pt by means of the ratio

$$R = \{[I_s(151) + I_{Pt}(150)]/I_{Pt}(237)\} - \{I_{Pt}(150)/I_{Pt}(237)\},$$

where I_i is the peak-to-peak height of the Auger transition of the ith element in the derivative mode spectrum (36).

According to Ku and Wynblatt (37), a SO_2-saturated Pt(110) surface is characterized by a ratio $R = 1.8$, corresponding to 0.21 monolayers, i.e., 0.21 SO_2 molecules per surface platinum atom. The low SO_2 concentration in the gas phase leads to $R \approx 0.15$, i.e., a coverage slightly below saturation. For the high SO_2 concentration in the gas phase, $R \approx 5$; this value is far higher than the one corresponding to a SO_2-saturated surface. This indicates that some sulfur-containing compounds, probably SO_3 or SO_4, have accumulated on the surface. Platinum is well known to catalyze oxidation of SO_2 in the presence of excess air (13).

No data could be found for the equilibrium adsorption of sulfur in the presence of SO_2, NO, and hydrocarbon. However, the fact that we observe a maximum activity for 1.6 ppm of SO_2, with an Auger peak ratio corresponding to a subsaturation coverage, suggests that the adsorption of sulfur dioxide is not hindered at all by the other gas components.

Another reason for the promoting effect might be that sulfur interferes with the formation of deactivating carbon deposits (38, 39).

At high SO_2 concentration in the gas phase (5×10^{-5} Torr), the rate of NO conversion strongly decreases, though the rate of i-C_4H_8O formation is still higher than in the absence of SO_2. This poisoning can be easily explained by a site-blocking effect toward NO chemisorption by atomic sulfur, SO_2, and oxidized SO_2 derivatives. The heat of desorption of SO_2 is equal to 225 kJ/mol, indicating strong adsorption (37). In our case, we believe that the effect of sulfur dioxide is twofold:

(i) SO_2 blocks the total oxidation of isobutene; this is a well-known effect of SO_2 upon hydrocarbon oxidation (12, 40, 41). This was also the conclusion made by Iwamoto *et al.*, who compared the influence of SO_2 on the decomposition of NO and on the oxidation of propene (13).

(ii) SO_2 poisons the reaction of NO with a surface intermediate.

Summers and Baron have also shown that SO_2 strongly inhibits NO and C_3H_6 conversion on a platinum/alumina-supported catalyst, the extent of the activity deterioration being dependent on the O_2 level (14). It could be that, under our slightly reducing conditions, when the level of SO_2 is too high, it is mainly converted into adsorbed S and H_2S, which block the surface.

The surface characterization of the sample performed at the most active stage of the reaction is in good agreement with the proposed mechanism. Low sulfur coverage induces an increase in the high BE contribution which has been ascribed to active intermediates. At higher sulfur coverages, the low BE contribution to the O 1*s* peak is increased, indicating poisoning of the surface by both sulfided and oxygenated species.

Nitrogen peaks of similar intensities were observed whatever the sulfur coverage. This suggests that, under our working conditions, sulfur affects the reactivity of hydrocarbons rather than the dissociation of NO.

CONCLUSION

This article reports a study, using mass spectrometric analysis, of the reaction between NO, i-C_4H_8 or i-C_4H_{10}, and O_2 on platinum together with XPS characterization of the Pt surface at different stages of the reaction. Evidence has been found to show that the reduction rate of NO correlates with the reactivity of the hydrocarbon with oxygen. The nature of the hydrocarbon, unsaturated or not, changes the role played by oxygen in the initiation of the reaction. With isobutane, the essential role of oxygen lies in the initiation stage of the reaction, by reacting with the hydrocarbon. With isobutene, oxygen is present throughout the reaction; it contributes to the formation of oxygenated intermediates and prevents surface deactivation by carbon. The determining role of reactive surface intermediates was confirmed by XPS characterization of the surface. An oxygen peak at around 532 eV was identified as a fingerprint of the catalytic activity of the surface. A low level of SO_2 in the gas phase, leading to a submonolayer of sulfur, promotes the conversion of NO in the presence of isobutene. This is a well-known effect in heterogeneous catalysis for “demanding” reactions. In our case, it resulted in a promotion of the selective oxidation of isobutene. Higher concentrations of SO_2 poison the Pt surface according to a classical steric poisoning phenomenon.

This combination of high-pressure reaction studies with surface characterization is a rather new approach for the deNO$_x$ reactions so far investigated. The present work has proved to be extremely fruitful in bringing new insight into the understanding of the mechanism of surface reactions involving NO and hydrocarbons.

ACKNOWLEDGMENT

This work was financially supported by the Swedish National Board of Technology (NUTEK).

REFERENCES

1. Zafiris, G. S., and Gorte, R. J., *Surf. Sci.* **276**, 86 (1992); Zafiris, G. S., and Gorte, R. J., *J. Catal.* **140**, 418 (1993).
2. Hamada, H., Kintaichi, Y., Sasaki, M., Ito, T., and Tabata, M., *Appl. Catal.* **64**, L1 (1990).

3. Kintaichi, Y., Hamada, H., Tabata, M., Sasaki, M., and Ito, T., *Catal. Lett.* **6**, 239 (1990).
4. Sato, S., Yu-u, Y., Yahiro, H., Mizuno, N., and Iwamoto, M., *Appl. Catal.* **70**, L1 (1991).
5. Zhang, G., Yamaguchi, T., Kawakami, H., and Suzuki, T., *Appl. Catal. B Environ.* **1**, L15 (1992).
6. Hamada, H., Kintaichi, Y., Sasaki, M., Ito, T., and Tabata, M., *Appl. Catal.* **69**, L15 (1991).
7. Li, Y., and Armor, J. N., *Appl. Catal. B Environ.* **1**, L31 (1992).
8. Obuchi, A., Ohi, A., Nakamura, M., Ogata, A., Mizuno, K., and Ohuchi, H., *Appl. Catal. B Environ.* **2**, 71 (1993).
9. Bennett, C. J., Bennett, P. S., Golunski, S. E., Hayes, J. W., and Walker, A. P., *Appl. Catal. A* **86**, L1 (1992).
10. Montreuil, C. N., and Shelef, M., *Appl. Catal. B Environ.* **1**, L1 (1992).
11. Ansell, G. P., Golunski, S. E., Hayes, J. W., Walker, A. P., Burch, R., and Millington, P. J., *Stud. Surf. Sci. Catal.* **96**, 577 (1995).
12. Monroe, R. D., Krueger, M. H., Beck, D. D., and D'Aniello, M. J., *Stud. Surf. Sci. Catal.* **71**, 593 (1991).
13. Iwamoto, M., Yahiro, H., Shundo, S., Yu-u, Y., and Mizuno, N., *Appl. Catal.* **69**, L15 (1991).
14. Summers, J. C., and Baron, K., *J. Catal.* **57**, 380 (1979).
15. Paál, Z., Schlögl, R., and Ertl, G., *Catal. Lett.* **12**, 331 (1992).
16. Peuckert, M., and Bonzel, H. P., *Surf. Sci.* **145**, 239 (1984).
17. Paál, Z., Muhler, M., and Schlögl, R., *J. Catal.* **143**, 318 (1993).
18. Wandelt, K., *Surf. Sci. Rep.* **2**, 1 (1982).
19. Gland, J. L., *Surf. Sci.* **93**, 487 (1980).
20. Anderson, J. A., and Rochester, C. H., *J. Chem. Soc. Faraday Trans.* **86**, 3809 (1990).
21. Paál, Z., and Schlögl, R., *Surf. Interface Anal.* **19**, 524 (1992).
22. Alikina, G. M., Davydov, A. A., and Sazonova, I. S., *Kinet. Katal.* **27**, 875 (1986).
23. Iwamoto, M., *Stud. Surf. Sci. Catal.* **54**, 121 (1990).
24. Nieuwenhuys, B. E., Siera, J., Tanaka, K., and Hirano, H., *Environ. Catal.* (J. N. Armor Ed.), ACS series, **115**, 552 (1994).
25. Kobylinski, T. P., and Taylor, B. W., *J. Catal.* **33**, 376 (1974).
26. Burch, R., Millington, P. J., and Walker, A. P., *Appl. Catal. B Environ.* **4**, 65 (1995).
27. Yogo, K., Umeno, M., Watanabe, H., and Kikuchi, E., *Catal. Lett.* **19**, 131 (1993).
28. Iwamoto, M., Yahiro, H., and Tanda, K., *Stud. Surf. Sci. Catal.* **37**, 219 (1988).
29. Nishijima, A., Kiyozumi, Y., Ueno, A., Kurita, M., Hagiwara, H., Sato, T., and Todo, N., *Bull. Chem. Soc. Jpn.* **52**, 3724 (1974).
30. Truex, T. J., Searles, R. A., and Sun, D. C., *Platinum Metal Rev.* **36**, 2 (1992).
31. Rostrup-Nielsen, J. R., *Stud. Surf. Sci. Catal.* **68**, 85 (1991).
32. Biswas, J., Bickle, G. M., Gray, P. G., Do, D. D., and Barbier, J., *Catal. Rev.-Sci. Eng.* **30**, 161 (1988).
33. Hayes, J. C., Mitshe, R. T., Pollitzer, E. L., and Homeier, E. H., *Prep. Div. Pet. Chem. Am. Chem. Soc.* **19**, 334 (1974).
34. Wise, H., McCarty, J., and Oudar, J., *in* "Deactivation and Poisoning of Catalysts" (J. Oudar and H. Wise, Eds.), p. 1. Dekker, New York, 1985.
35. Oudar, J., Pinol, S., Pradier, C. M., and Berthier, Y., *J. Catal.* **107**, 445 (1987).
36. Bonzel, H. P., and Ku, R., *J. Chem. Phys.* **58**, 4617 (1973).
37. Ku, R. C., and Wynblatt, P., *Appl. Surf. Sci.* **8**, 250 (1981).
38. Sachtler, W. M. H., *J. Mol. Catal.* **25**, 1 (1984).
39. Augustine, S. M., Nacheff, M. S., Tsang, C. M., Butt, J. M., and Sachtler, W. M. H., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. III, p. 1190. Chem. Institute of Canada, Ottawa, 1988.
40. Mabilon, G., Durand, D., and Courty, Ph., *Stud. Surf. Sci. Catal.* **96**, 775 (1995).
41. Yao, H. C., Stephen, H. K., and Gandhi, H. S., *J. Catal.* **67**, 231 (1981).