NO Reduction by CO over Pt/Al$_2$O$_3$ and Pt/CeO$_x$/Al$_2$O$_3$: Oscillations and Deactivation

Y. J. Mergler and B. E. Nieuwenhuys[1]

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

CO/NO reactions have been studied over two catalysts, Pt/CeO$_x$/Al$_2$O$_3$ and Pt/Al$_2$O$_3$, under net reducing conditions. The Pt/Al$_2$O$_3$ catalyst deactivated with time at 400°C whereas the Pt/CeO$_x$/Al$_2$O$_3$ catalyst showed oscillations in the reaction rate at this temperature. The oscillations had periods of 18 min. By using Fourier transform infrared spectroscopy, an attempt was made to reveal the species that inhibits the reaction over Pt. It is suggested that CeO$_x$ provides dissociation centers for NO under conditions where NO dissociation is hindered by the inhibiting species on the Pt sites.   © 1996 Academic Press, Inc.

INTRODUCTION

Three-way catalysts for automobiles operate under varying conditions of temperature and gas-phase composition. For example, the exhaust gas varies from rich gas mixtures during the cold start to lean mixtures during high driving speeds. The lambda sensor, installed to control the air/fuel ratio, has a certain response time leading to periodic changes in the gas-phase composition. By studying oscillating reactions, fundamental knowledge can be gained about processes that are taking place on the surface of catalysts or single crystals (1–4).

Catalytic reactions show oscillatory behavior only under special conditions. It is necessary that the reactions be carried out far from equilibrium. When a flow system is used, the constant supply of reactants keeps the system from reaching thermodynamic equilibrium. The products formed during the reaction have to influence their own rate of formation. In other words, feedback is necessary. For example, feedback may be supplied by the generation of sites on the catalyst surface by the reaction, which allows further reaction to take place. Autocatalytic behavior then plays an important role. The last requirement for oscillations is the need for bistability. The system must be able to exist in two or more steady states. This may be caused by a different structure or composition of the catalyst during these steady states.

To account for the observed phenomena of oscillations, several mechanisms were suggested (5–17). A brief description of these mechanisms follows. In one model the oscillations are a result of overheating of the catalyst particles due to the exothermicity of the reaction. Especially for supported catalysts this mechanism may be operative since the support usually consists of insulating materials like SiO$_2$ and Al$_2$O$_3$ which cannot conduct the heat properly. Wolf *et al.* (5–10) found, by studying the spatial temperature distribution of supported catalysts with Fourier transform infrared (FT-IR) spectroscopy, that the temperature of the catalyst particles is not uniform during the reaction. Usually, the initiation of the exothermic reaction starts on a defect site or an impurity, followed by local heat accumulation on the catalyst. The reaction proceeds until the temperature becomes too high for the reactant molecules to adsorb on the surface. This slows down the reaction and can lead to a temperature drop until the cycle starts again, for example, initiated by reaction over defect sites or impurities.

A second mechanism was proposed for oscillations under isothermal conditions, observed for single-crystal surfaces at low partial pressures. Heat production can be neglected for the reactions at low partial pressures over heat-conducting single crystals. Aldhoch and Lintz (11) and Ertl (4) explained the observed oscillations by the occurrence of surface structural changes of the single-crystal surface. The Pt(100) surface with a (1 × 1) structure is active in CO oxidation by O$_2$ (4). The reaction occurs until the CO coverage drops below a critical value required for the maintenance of the (1 × 1) structure. The surface then relaxes to the (5 × 20) structure, which is almost inactive in O$_2$ dissociation and, hence, in CO oxidation. As a result, the CO coverage builds up, leading to a phase transformation into the more active (1 × 1) structure.

A third model was proposed by Sales, Turner, and Maple (STM model) (13). Cyclic oxidation–reduction of the surface was suggested to account for the effects observed during CO oxidation by O$_2$ over supported metal catalysts. The reported oscillations showed periods of several minutes to 1 h. Oxygen adsorption also leads to bulk oxidation.

[1] To whom correspondence should be addressed. Fax: 31-71-5274451.

A strongly bound oxygen species may only be removed slowly by CO. The rates of CO_2 formation on clean and oxidized metal must differ to a great extent to explain the oscillations. Blocking of the active metal surface by carbon was proposed by Burrows *et al.* (12) for CO/O_2 reactions over a Pt foil.

A vacancy model was suggested by Van Tol *et al.* (14–17) for NO reduction reactions over single-crystal surfaces of Pt. O_a plays a key role in this model. In the H_2/NO reaction the dissociation of NO is inhibited by a high surface coverage of NO. Due to desorption of NO or reaction between O_a and H_a, some free sites (vacancies) are created. More NO molecules can now dissociate, leading to a fast reaction from N_a, H_a, O_a to N_2, H_2O, NH_3. This step is autocatalytic. As the reaction proceeds, the concentration of O_a on the surface increases, which inhibits further NO dissociation because the strongly bound O atoms on Rh are only slowly removed by hydrogen.

On studying the CO/NO reaction over two catalysts of interest for automotive catalysis, namely, $Pt/CeO_x/Al_2O_3$ and Pt/Al_2O_3, oscillations in reactant and product gases were obtained for the $Pt/CeO_x/Al_2O_3$ catalyst with net reducing gas mixtures. The activity of Pt/Al_2O_3 decreased under these conditions. In this paper we suggest a possible explanation for the observed phenomena.

The two possible reaction pathways for reducing NO with CO are

$$2CO + 2NO \rightarrow N_2 + 2CO_2, \qquad [1]$$

$$CO + 2NO \rightarrow N_2O + CO_2. \qquad [2]$$
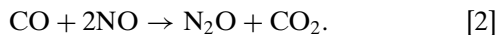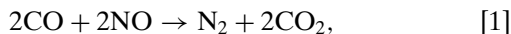
N_2O is believed to be an important intermediate product in the CO/NO reaction (18–20). The following reaction may also proceed:

$$CO + N_2O \rightarrow N_2 + CO_2. \qquad [3]$$

EXPERIMENTAL

The catalysts were obtained from Degussa. The Pt loading of the Pt/Al_2O_3 catalyst was 0.4 wt%. The $Pt/CeO_2/Al_2O_3$ catalyst consisted of 0.4 wt% Pt and about 29 wt% CeO_2. The very finely powdered catalysts were directly used after an oxidation or a reduction as pretreatment, both for 1 h at 400°C in, respectively, air or pure H_2 (Hoekloos). The measurements were performed in an atmospheric flow apparatus. The flow could be adjusted by mass flow controllers to a maximum flow rate of 40 ml/min. The diameter of the reactor was 20 mm and the height of the catalyst bed, with 0.2 g catalyst, was 5 mm. The gases used were supplied by AGA and Hoekloos and contained 4 vol% NO/He and 4 vol% CO/He. Oscillations were obtained with CO:NO ratios of 3:1. The temperature was raised at 3°C/min from room temperature to 410°C. A chromel–alumel thermocouple was embedded directly in the sample and the output was used as the feedback signal to regulate an oven made of heating tape wrapped around an aluminum gasket, which allowed a rapid temperature response.

Product and reactant analyses were performed by means of a quadrupole mass spectrometer (Masstorr DX, VG Instruments). Every 45 s the partial pressures of the reactants and products were recorded. These partial pressures were normalized by dividing them by the partial pressure of NO at $t = 0$. The partial pressures were plotted against the temperature or the number of measurements. Each measurement lasted about 45 s. Since the masses of CO/N_2 and CO_2/N_2O are equal and our mass spectrometer was not sensitive enough to monitor masses 14 of N and 16 of O accurately, only the differences in activity of the two Degussa catalysts could be measured.

The fragmentation of CO_2 and N_2O was measured: CO_2, as well as N_2O, contributed some 10% to the intensity of the mass 28 signal (CO and N_2). The contribution of N_2O to mass 30 (NO) was found to be about 15%. The signal for mass 28 was corrected for the contribution of the fragments of CO_2 and N_2O. The signal for mass 30 was not corrected, since the contribution of N_2O to the signal of mass 44 could not be determined accurately. When only reaction [2] is considered, half of the signal of mass 44 should be N_2O. However, in practice we cannot determine the selective contributions of reactions [1] and [2] with our mass spectrometer.

To obtain relevant information concerning the mechanism of the oscillations, FT-IR spectroscopy was used. However, these FT-IR measurements could be performed only in a batch reactor.

For FT-IR measurements self-supporting pellets were pressed with a diameter of 10 mm. The pellets weighed about 6 mg. The catalyst was reduced *in situ* at 300°C in 100 mbar H_2, prior to the measurements. Background spectra were taken at room temperature, and 100, 200, 300, 350, and 400°C at 10^{-5} mbar. Sample spectra were recorded at the temperatures mentioned in a mixture of 1 mbar NO and 3 mbar CO. The spectra were taken with a resolution of 4 cm^{-1}. To improve the signal/noise ratio, the average of 32 spectra was taken to form one spectrum. A Galaxy 2020 (Mattson) was used for the IR measurements.

The catalysts were further characterized by CO chemisorption in an atmospheric flow apparatus. After an *in situ* reductive pretreatment the catalyst was cooled to room temperature in the H_2 flow. CO was injected until saturation was reached. H_2 was used as a carrier gas: for our catalysts, this leads to the same results as using He as carrier gas. Table 1 shows the measured dispersions of the catalysts based on the assumption that one CO molecule is adsorbed per surface Pt metal atom in CO chemisorption measurements.

TABLE 1

Metal Dispersion of the Catalysts

Catalyst	Pt (wt%)	CeO_2 (wt%)	Dispersion (%)
Pt/Al_2O_3	0.4	—	68
$Pt/CeO_x/Al_2O_3$	0.4	29	43

RESULTS

Oscillations and Activity Decrease

The CO/NO reaction was studied over $Pt/CeO_x/Al_2O_3$ and Pt/Al_2O_3 with gas mixtures that were net reducing, stoichiometric, or oxidizing. Interesting phenomena were observed for these catalysts, especially at CO/NO ratios of 3:1. These results are reported in this paper.

Figure 1 shows the variations in partial pressures of the reactants and products of the $Pt/CeO_x/Al_2O_3$ catalyst with time, following a reductive pretreatment. Around 400°C the concentrations of the products and reactants start to oscillate. The intensities of the CO and NO signals oscillate in phase, and out of phase, with that of the reaction products with mass 44. The NO signal seems to show two maxima in one period.

Figure 1 shows that around measurement number 120, in which case the temperature was about 275°C, minima in the signals of mass 28 (CO/N_2) and mass 30 (NO) were accompanied by an increase in the signal of mass 44 (CO_2/N_2O).

For reaction [1], where two CO and two NO molecules react to N_2 and two molecules of CO_2, one can calculate that 2 molecules of mass 28 should disappear, while one molecule of mass 28, namely N_2, is formed. For every NO molecule that disappears, one CO_2 molecule is formed. On careful study of the mass balances at 275°C it was observed that relatively more CO was used and that more product was formed! This effect was also visible around 275°C with a stoichiometric CO/NO ratio over a $Pt/CeO_x/Al_2O_3$ catalyst after an oxidative pretreatment, as is shown in Fig. 2. Above 360°C the conversion is complete and the mass balance is as should be expected, showing that only reaction [1] is proceeding at these high temperatures.

Figure 3 shows the CO/NO reaction with CO:NO = 3:1 over Pt/Al_2O_3. This catalyst also showed the minima and maxima around 275°C, as observed for $Pt/CeO_x/Al_2O_3$ (Figs. 1 and 2). Another important finding was the deactivation of the Pt/Al_2O_3 catalyst at 400°C as was observed by a decrease in the signal of mass 44 and an increase in the signals of mass 28 and 30, almost up to their original value! At 400°C the reaction rate between CO and NO was initially very fast. However, NO conversion slowly decreased at this temperature and after 1 h the catalyst was almost inactive.

Figure 4 shows that on mainpulation of the reactant gases at 400°C over the $Pt/CeO_x/Al_2O_3$ catalyst the oscillation is damped, while restoring the original reactant gas ratio led to a restart of the oscillatory behavior of the $Pt/CeO_x/Al_2O_3$ catalyst.
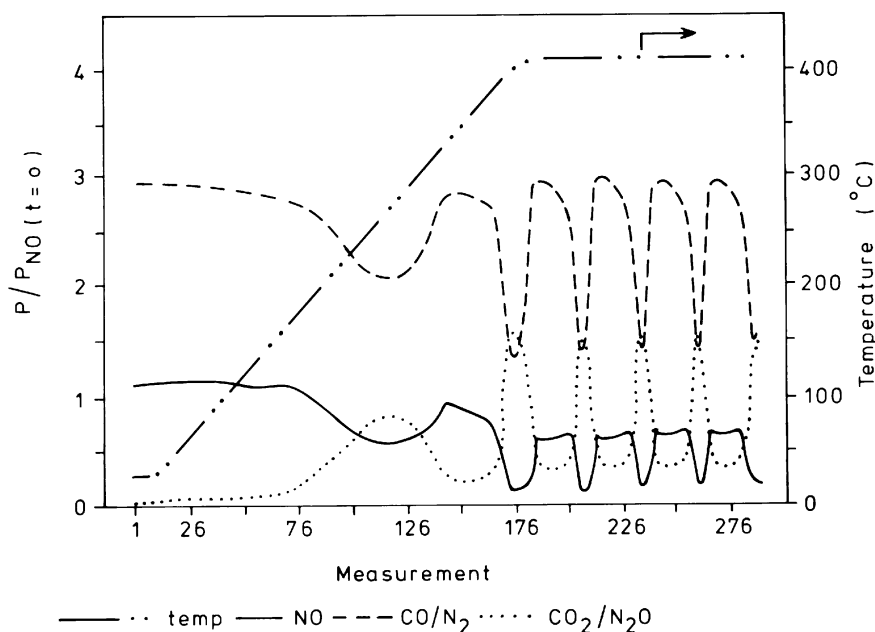

FIG. 1. Oscillations in the partial pressures of CO/N_2, NO, and CO_2/N_2O (all normalized on the partial pressure of NO at $t = 0$) during the reaction between CO and NO with CO:NO = 3:1 over $Pt/CeO_x/Al_2O_3$, after a reductive pretreatment. Every 45 s, a measurement was performed; the temperature was raised at a rate of 3°C/min.
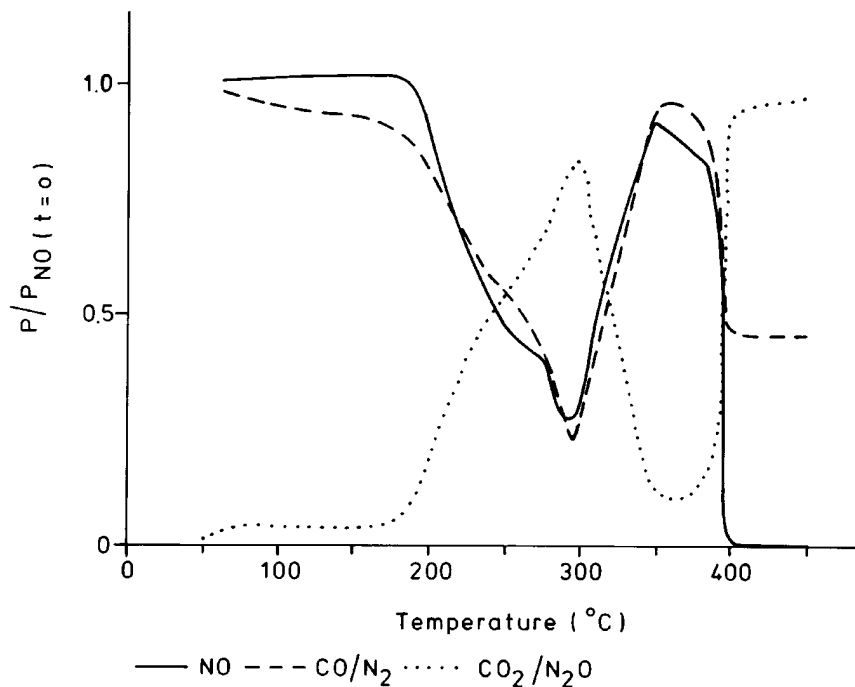
FIG. 2. Variation of the partial pressures of CO/N$_2$, NO, and CO$_2$/N$_2$O (all normalized on the partial pressure of NO at $t = 0$) during the reaction between CO and NO with CO : NO $= 1 : 1$ over Pt/CeO$_x$/Al$_2$O$_3$, after an oxidative pretreatment.

Infrared Spectra

Figure 5 shows the FT-IR spectra on the adsorption of CO and a mixture of CO and NO on Pt/CeO$_x$/Al$_2$O$_3$ after a reductive pretreatment. The gas ratio of CO/NO was 3. For adsorption of CO at 100°C, bands of CO linearly bound to Pt at 2070 cm^{-1} and carbonate bands in the region 1700–1300 cm^{-1} were seen. When 1 mbar NO was added to the IR cell that already contained 3 mbar CO, no additional bands appeared at 100°C. The assignment of the carbonate bands is rather difficult and is further complicated when NO is present. NO may lead to the formation of nitrate-
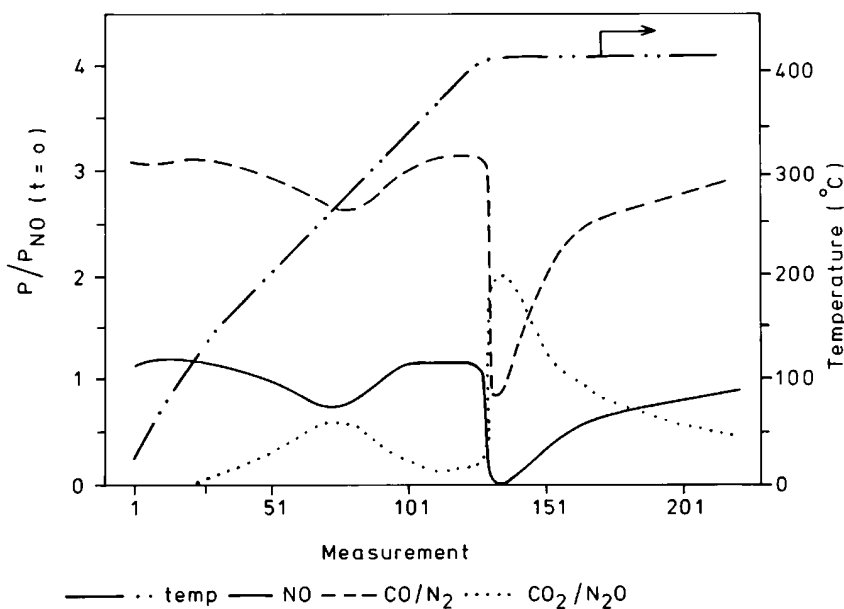

FIG. 3. Deactivation of Pt/Al$_2$O$_3$ during the reaction between CO and NO with CO : NO $= 3 : 1$, after a reductive pretreatment. The partial pressures of the masses are all normalized on the partial pressure of NO at $t = 0$. Every 45 s, a measurement was performed. The temperature was raised at 3°C/min.
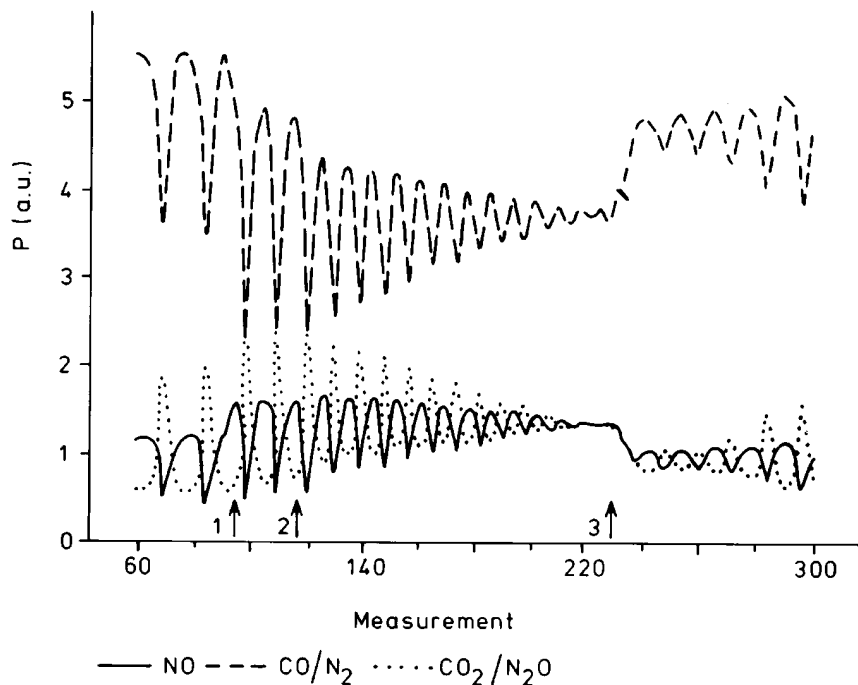
FIG. 4. Manipulation of the gas ratio of CO/NO during the CO/NO reaction over $Pt/CeO_x/Al_2O_3$ at $400°C$. All the partial pressures are normalized on the partial pressure of NO at $t=0$. At measurement 90, the CO/NO gas ratio was decreased from 3 to 2. At measurement 117, it was further decreased to 1.67. At measurement 230, the original CO/NO gas ratio of 3 was restored. Every 45 s, a measurement was performed; the temperature was kept constant at $400°C$.

and nitrite-type species, which show bands in the same wavenumber region as the carbonate-type species. When the temperature was raised to $200°C$, bands at 2178, 2228, and $2253 cm^{-1}$ developed, as can be seen in Fig. 5c. These bands were assigned, respectively, to isocyanate bound to Pt and to Al_2O_3. Isocyanate bound to Al_2O_3 shows a doublet (21, 22). It cannot be excluded a priori that adsorbed N_2O also contributes to the $2230 cm^{-1}$ band. Bands at 2235 and $1255 cm^{-1}$ have been reported for NO adsorption on ceria and assigned to adsorbed N_2O (23). Adsorbed N_2O is only weakly bound to ceria. In our case the 2230 and $2250 cm^{-1}$ bands are very stable even at $250°C$. Hence, it is unlikely that N_2O will contribute significantly to the band near $2230 cm^{-1}$ which is assigned here to isocyanate on alumina. We cannot exclude, however, that an isocyanate species bound to CeO_x is also contributing to the observed 2250 or $2230 cm^{-1}$ band. Isocyanate bands on metal oxides have band positions in the range 2200 to $2260 cm^{-1}$ (21, 22, 24, 25). At $250°C$ these latter bands increased in intensity and a small band around $1460 cm^{-1}$ was found, ascribed to the symmetric stretch of isocyanate. When the temperature was further increased, the band of linearly bound CO on Pt disappeared gradually. A new band around $2100 cm^{-1}$ appeared at $400°C$, accompanied by a broad band around $2000 cm^{-1}$. The Pt–NCO band at $2180 cm^{-1}$ was visible as a shoulder. After evacuation at $100°C$ (Fig. 5h) the isocyanate band of Al_2O_3 was again resolved into two bands.

Figure 6 shows the spectra on the adsorption of CO and NO on Pt/Al_2O_3. CO linearly bound to Pt and the isocyanate species bound to Al_2O_3 were clearly visible, together with carbonate and nitrate bands below $1700 cm^{-1}$. However, a band of isocyanate bound to Pt was lacking, as can be seen in Figs. 6c to j. Above $300°C$, the band of CO linearly bound to Pt disappeared. Figures 6h to k show a new band around $2115 cm^{-1}$, which arose at $400°C$. This band increased in intensity with time. The band at $2115 cm^{-1}$ appeared to be very stable, even on introduction of 1 mbar O_2 at $400°C$ (Figs. 6j and k).

An almost stoichiometric CO/NO gas mixture was added to a prereduced $Pt/CeO_x/Al_2O_3$ catalyst and the resulting spectra are shown in Fig. 7. On adsorption of CO and NO at $350°C$ (Fig. 7a) bands of CO linearly bound to Pt at $2050 cm^{-1}$, isocyanate bound to Pt at $2180 cm^{-1}$, and isocyanate bound to Al_2O_3 at 2245 and $2234 cm^{-1}$ were seen, together with bands of carbonate and nitrate species below $1700 cm^{-1}$. After 10 min at $350°C$, only the carbonate, nitrate, and isocyanate bands were visible. Introduction of almost 4 mbar CO at $350°C$ (Fig. 7d) led to the reappearance of linearly bound CO to Pt. After 7 min the isocyanate bands again increased in intensity. After cooling to room temperature and evacuation, the bands of isocyanate bound to Pt and Al_2O_3 were seen. Figure 7g also shows the $2046 cm^{-1}$ band of CO linearly bound to Pt and a rather broad band around $2000 cm^{-1}$. Figure 7h shows the spectrum
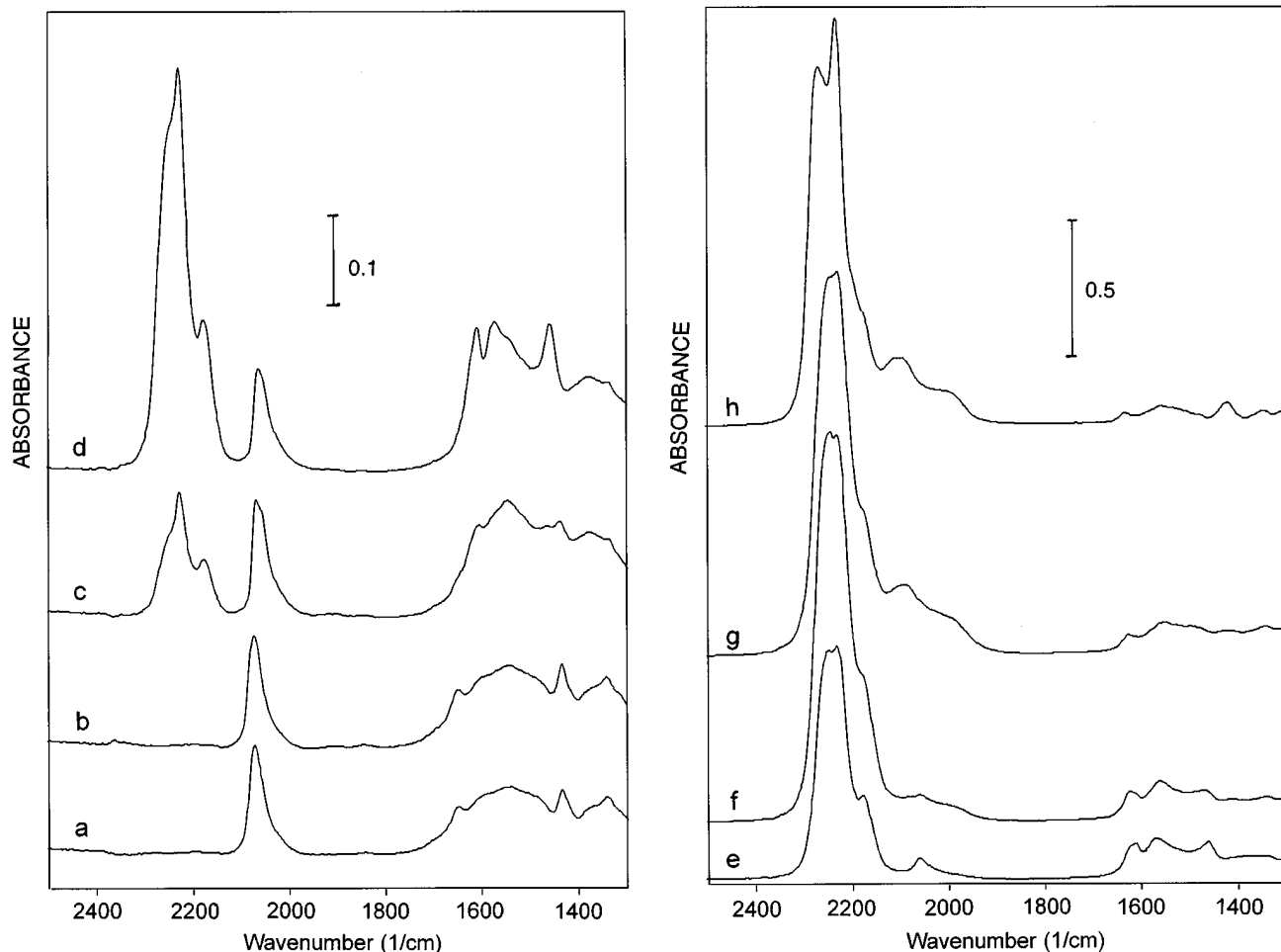
FIG. 5. IR spectra of Pt/CeO$_x$/Al$_2$O$_3$ after a reductive pretreatment. (a) Addition of 3 mbar CO at 100°C. (b) Addition, of 1 mbar NO at 100°C. (c–h) Mixture of 3 mbar CO + 1 mbar NO at (c) 200°C, (d) 250°C, (e) 300°C, (f) 350°C, (g) 400°C, and (h) 100°C, evacuated to 2 × 10^{-5} mbar.

after the addition of 10 mbar O$_2$ at room temperature. The band of the linearly bound CO species disappeared directly. The intensity of the isocyanate species diminished above 300°C, and at 350°C hardly any isocyanate could be detected. No band around 2100–2115 cm^{-1} was detected in this experiment.

CO Oxidation with O$_2$ after Oscillations

CO oxidation over Pt/Al$_2$O$_3$ and Pt/CeO$_x$/Al$_2$O$_3$ has been described recently by Serre *et al.* (26). In this work the reaction was not studied in detail. The reaction was studied only to obtain additional information on the nature of the deactivation and the oscillations in reaction rate observed for the CO + NO reaction for Pt/Al$_2$O$_3$ and Pt/CeO$_x$/Al$_2$O$_3$, respectively.

The activity of the Pt/CeO$_x$/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts in CO oxidation with O$_2$ was measured directly after the oscillation/deactivation reactions in CO/NO = 3 : 1, and compared with freshly reduced Pt/CeO$_x$/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalyst. Figures 8 and 9 show the behavior in CO

oxidation by O$_2$ of the Pt/CeO$_x$/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts, respectively. The catalysts were measured twice: once directly after the CO/NO reactions and again after cooling to room temperature under the reactant CO/O$_2$ flow. An oxidizing gas mixture was used with a CO/O$_2$ gas ratio of 1 : 1. Figures 8 and 9 show that the temperature of 50% CO conversion ($T_{50\%}$) is higher for the used catalyst than for the freshly reduced catalysts. The $T_{50\%}$ of the the second measurement of the catalysts lay between the value of $T_{50\%}$ of the freshly reduced catalyst and the value of $T_{50\%}$ of the first measurement directly after the CO/NO reactions. Due to the oxidizing CO/O$_2$ gas mixture it is likely that the catalysts were slightly oxidized after the first measurement directly after CO/NO reactions. The second measurement may then take place over a more oxidized catalyst.

DISCUSSION

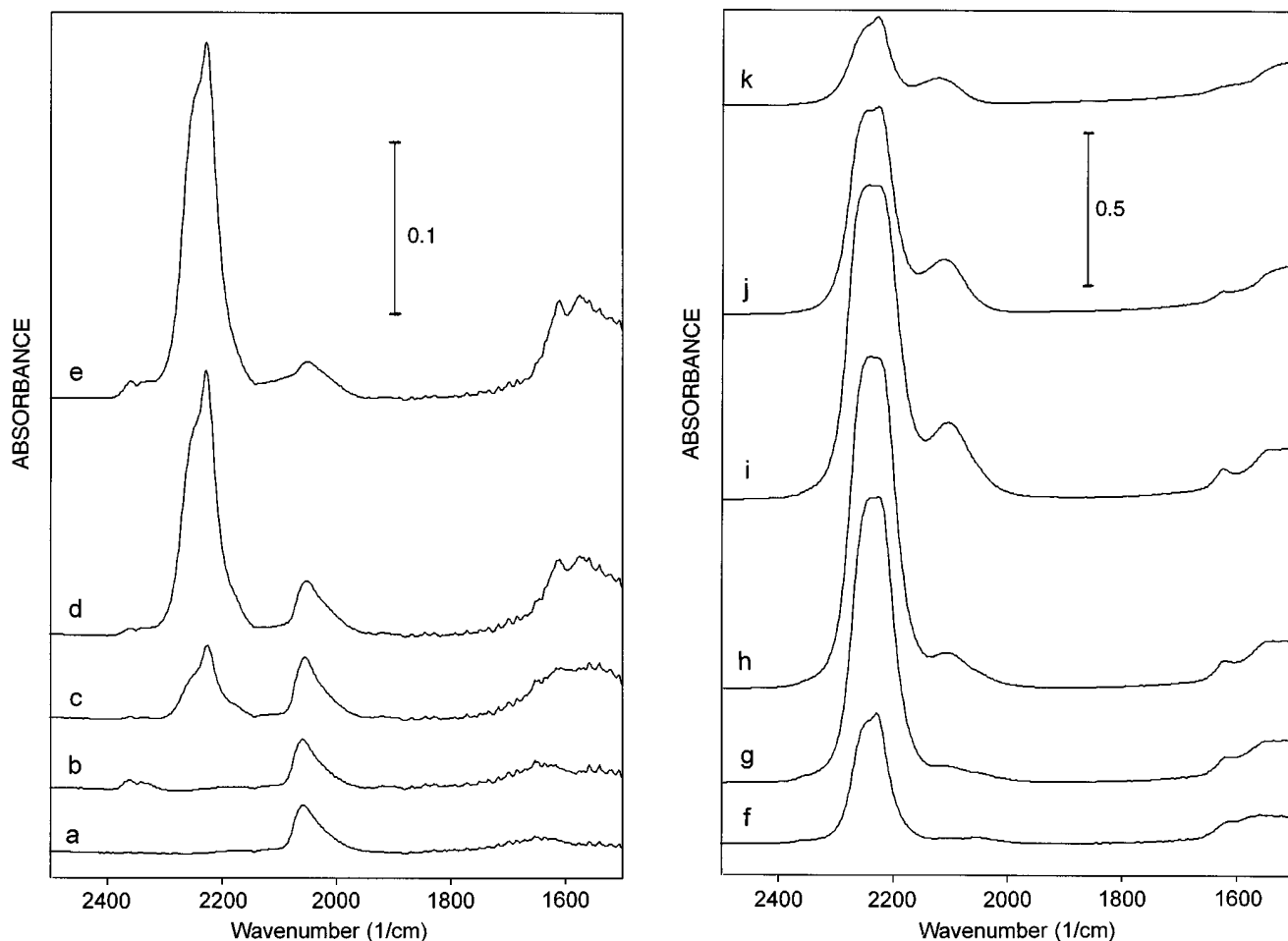The relevant results of this study are the observed oscillations in the rate of the CO/NO reaction over Pt/CeO$_x$/Al$_2$O$_3$

FIG. 6. IR spectra of Pt/Al_2O_3 after a reductive pretreatment. (a) Addition of 3 mbar CO at $100°C$. (b) Addition of 1 mbar NO at $100°C$. (c–j) Mixture of 3 mbar CO and 1 mbar NO at (c) $200°C$, (d) $250°C$, (e) $300°C$, (f) $350°C$, (g) $400°C$, $t = 0$ min, (h) $400°C$, $t = 7$ min, (i) $400°C$, $t = 36$ min, and (j) $400°C$, evacuated to 1×10^{-1} mbar. (k) Addition of 1 mbar O_2, $t = 0$ min, $400°C$, 16 min.

under conditions at which the Pt/Al_2O_3 catalyst deactivates with time. Apparently, the addition of ceria results in the oscillatory behavior and in maintaining a high activity. Ceria is added to the three-way catalyst for a number of reasons, including improved thermal stability of the support, and it serves as an oxygen buffer due to transitions between Ce(III) and Ce(IV). In addition, direct promoter effects of ceria have also been reported. For a recent discussion of the roles of ceria, refer to Ref. (26).

Possible Models

To our knowledge, this is the first report of oscillatory behavior for CO/NO reactions over Pt catalysts with a large excess of CO. Usually, oscillations in NO reduction reactions over Pt are observed only with excess NO (5–10, 16), or with a slight excess of CO (27–29).

Changes in surface structure and morphology of the catalyst particles can take place under the reaction conditions used (30), resulting in changes in activity and, possibly, oscillations. In our opinion, it is not very likely that these

structural changes will lead to complete deactivation of the catalyst. Since the deactivation of Pt/Al_2O_3 and the oscillatory behavior of $Pt/CeO_x/Al_2O_3$ are probably related processes, we believe that the oscillatory behavior is not merely caused by surface structural changes.

Steep rises in temperature, a model suggested by Wolf *et al.* (5–10), cannot account for the results obtained in CO/NO reactions with excess CO as observed by us. No indications at all were found of changes in the temperature. About every 45 s the partial pressures of the gases and the temperature were measured, but no temperature rise was seen. If heat production is that important, some temperature effects should have been noted, since the periods of oscillation last at least 18 min. The initial rate and, hence, the heat production of the reaction should be rather similar for the Pt/Al_2O_3 and $Pt/CeO_x/Al_2O_3$ catalysts, but oscillations were found only for the $Pt/CeO_x/Al_2O_3$ catalyst.

The CO/NO reaction over Pt/Al_2O_3 does not show oscillatory behavior as was shown in Fig. 3 but, surprisingly, a deactivation with time. It is tempting to correlate the
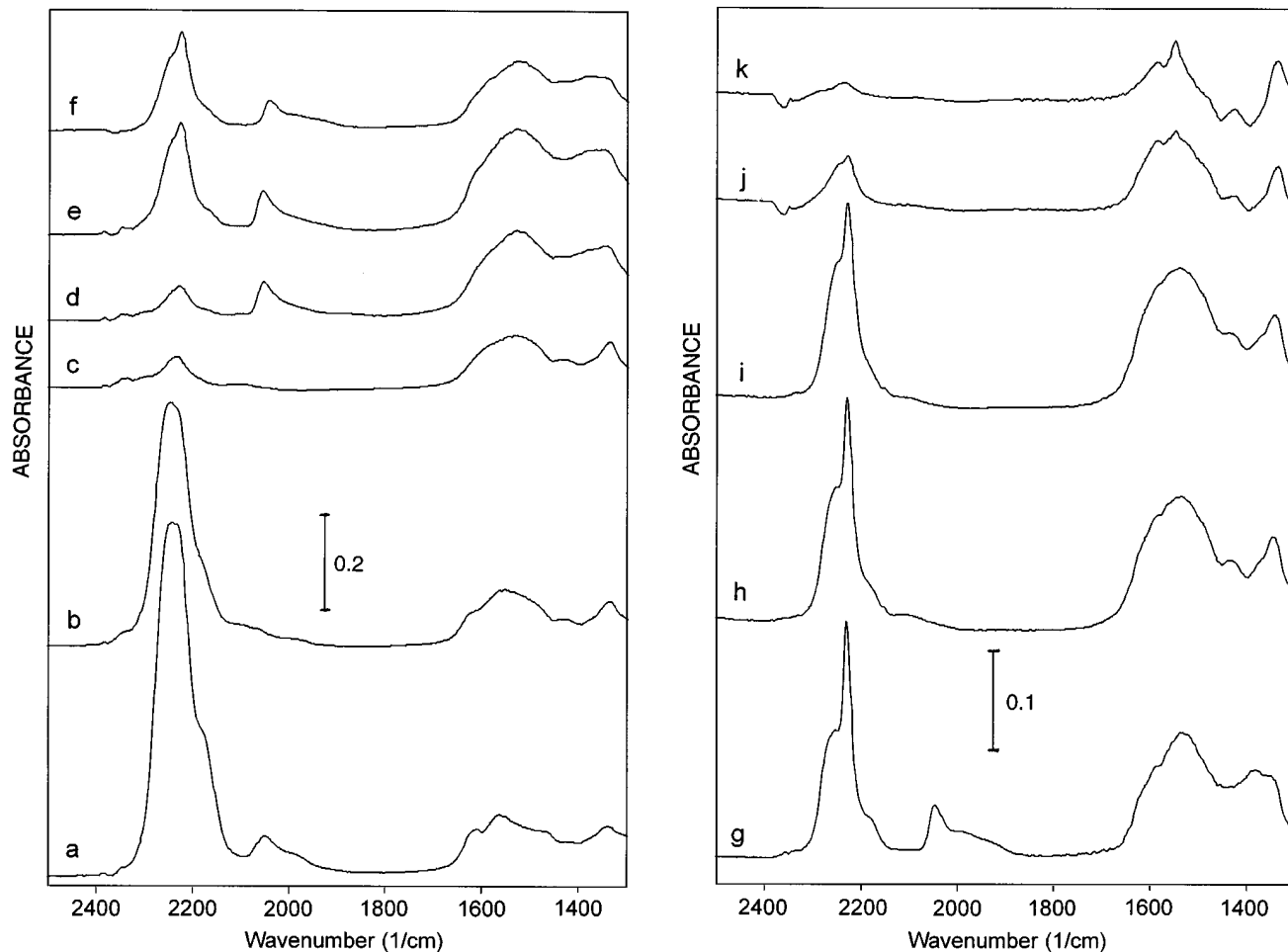
FIG. 7. IR spectra of Pt/CeO$_x$/Al$_2$O$_3$ after a reductive pretreatment. (a–c) Addition of 5 mbar CO and 4.5 mbar NO at (a) 350°C, $t = 0$ min, (b) 350°C, $t = 5$ min, and (c) 350°C, $t = 10$ min. (d–g) Addition of 3.75 mbar CO at (d) 350°C, $t = 0$ min, (e) 350°C, $t = 7$ min, (f) 350°C, evacuated to 4×10^{-5} mbar, and (g) cooled to room temperature and evacuated to 4×10^{-6} mbar. (h–k) Addition of 10 mbar O$_2$ at (h) room temperature, (i) 200°C, (j) 300°C, and (k) 350°C.

deactivation of the Pt/Al$_2$O$_3$ catalyst with the occurrence of oscillations over the Pt/CeO$_x$/Al$_2$O$_3$ catalyst. The only models that may provide an explanation are those in which an inhibition effect, by the presence of an adsorbate, is suggested. This leaves the oxidation (STM) model, in which the oscillations are the result of periodic transitions between an active and a less active phase, such as an oxidized catalyst, and models in which the oscillations are ascribed to impurities or other inhibitors (12, 31).

Although several authors believe that distinct models can account for the observed oscillations over different catalysts (27–29) we are inclined to think that the same model, namely, inhibition by the presence of a less active adsorbate, is responsible for the observed oscillations over Pt/CeO$_x$/Al$_2$O$_3$ as well as the deactivation of Pt/Al$_2$O$_3$.

By using IR spectroscopy, we have tried to reveal which species may be responsible for the deactivation of the Pt/Al$_2$O$_3$ catalyst and the oscillations in CO/NO reaction

rates found for the Pt/CeO$_x$/Al$_2$O$_3$ catalyst. These results are discussed in a later section.

Discrepancies in the Mass Balance

As was shown under Results (Figs. 1–3), there are discrepancies in the mass balances of mass 28, 30, and 44. Several possible explanations are discussed in this section.

Reduction by CO. For example, when the mass balance around 275°C was considered over Pt/CeO$_x$/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ it was found that relatively more mass 28 disappeared and that more product (mass 44) was formed. To ascribe this phenomenon to further reduction by CO of the Pt/Al$_2$O$_3$ and Pt/CeO$_x$/Al$_2$O$_3$ catalysts is rather unlikely since the catalysts were reduced in H$_2$ prior to the CO/NO measurements.

Boudouard reaction. The discrepancies in the mass balance of Pt/CeO$_x$/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ in Figs. 1 and 3,

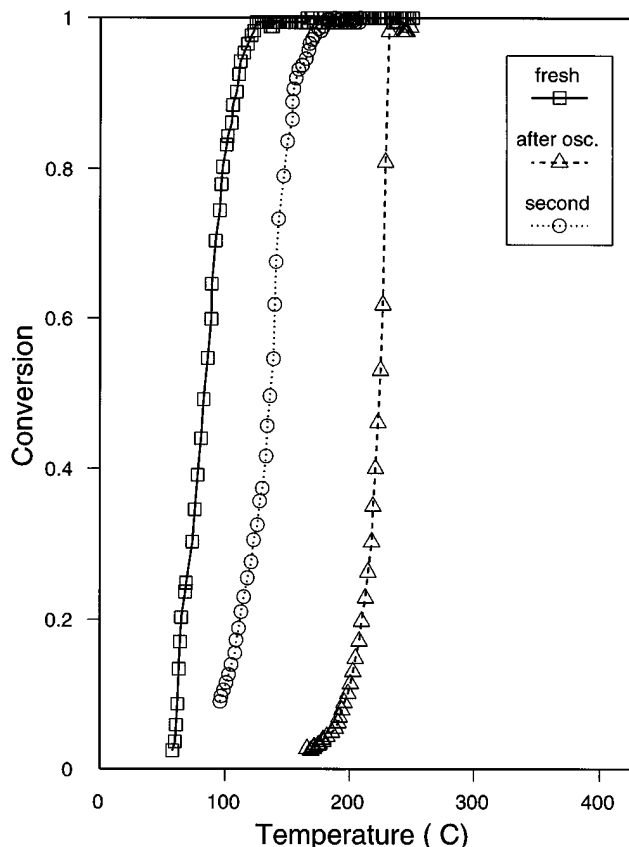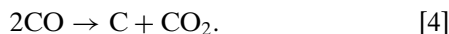**FIG. 8.** CO/O_2 reaction with CO:$O_2 = 1:1$ over Pt/CeO$_x$/Al$_2$O$_3$ after a reduction (fresh), directly after the experiments in CO/NO gas mixtures with a CO/NO gas ratio of 3:1 without any treatment (after osc.), and measured for the second time without any treatment (second).

respectively, might be explained by the assumption that the following reaction takes place:

$$2CO \rightarrow C + CO_2. \qquad [4]$$

However, numerous studies indicate that this reaction (the Boudouard reaction) cannot take place over Pt catalysts (12, 32). No carbonaceous layer could be detected with AAS after reactions. No CH$_4$ was detected when the catalyst was heated in a H$_2$ flow after the CO/NO reactions. Thus, the decomposition of CO was ruled out.

CO or N$_a$, or both, remain on the catalyst surface. After an oxidative pretreatment and a CO/NO ratio of unity (Fig. 2), the NO and product balance seemed to be as would be expected according to reaction [1] or [2]. Every NO molecule that disappeared generated one product molecule. Now the mass balance of mass 28 alone showed a discrepancy. The decrease in mass 28 should be half the decrease of mass 30 according to reaction [1] or [2]. The discrepancy could be explained by the assumption that either CO or N$_a$ (29), or both, is held on the catalyst surface. Tanaka *et al.* found that N overlayers are not easily formed

on Pt(100), in contrast to Pd(100) and Rh(100) (33). CO can be held as carbonaceous species on the alumina surface (34). However, as mentioned earlier, no indication of a carbonaceous layer was found. Formation and decomposition of carbonates cannot explain the observed discrepancies in the mass balance after a reductive pretreatment of the catalysts. It might be possible that the nitrogen is held as nitrate species on the surface. Assumption that a nitrate species inhibits the reactions over the prereduced Pt/Al$_2$O$_3$ and Pt/CeO$_x$/Al$_2$O$_3$ catalysts is also unlikely, when the mass balance of Figs. 1 and 3 is regarded. Another candidate may be formation of isocyanates, as will be discussed in the next section.

Which Species is Responsible for the Deactivation/Oscillations?

Isocyanate. To elucidate the question of the inhibiting species, FT-IR measurements were performed. It should be kept in mind that the FT-IR measurements were performed in the batch mode. Hence, the information obtained concerning the presence of adsorbates cannot be directly
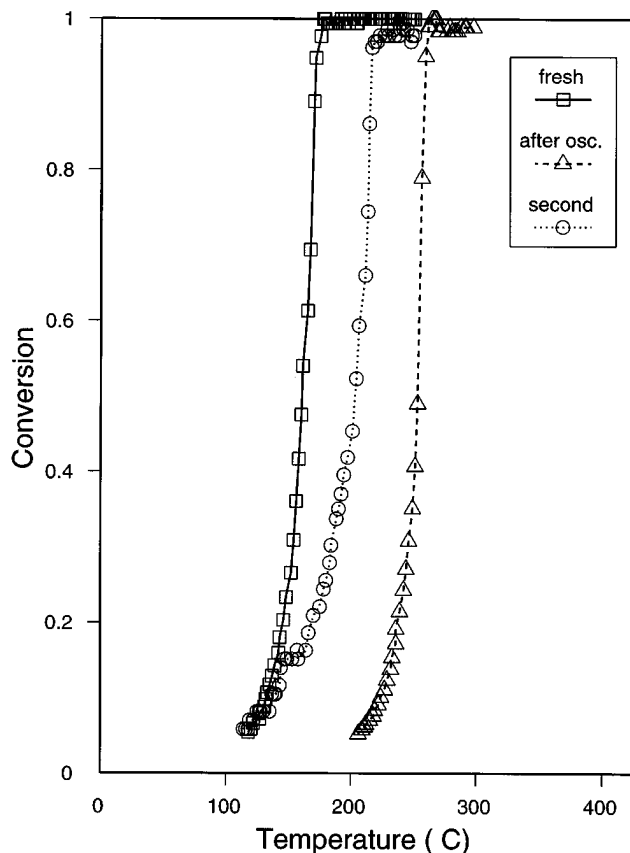

FIG. 9. CO/O_2 reaction with CO:$O_2 = 1:1$ over Pt/Al$_2$O$_3$ after a reduction (fresh), directly after the experiments with CO/NO gas mixtures in which the CO/NO ratio was 3:1 without any treatment (after osc.), and measured for the second time without any treatment (second).

applied to the catalysts studied in the flow reactor. However, the FT-IR results can still provide useful information on the role of ceria by comparison with the FT-IR spectra of Pt/Al$_2$O$_3$ and Pt/CeO$_x$/Al$_2$O$_3$ and on the nature of stable species which might be responsible for the observed deactivation of Pt/Al$_2$O$_3$.

A possible candidate as inhibitor, which should be considered, is the isocyanate species (35–37). In the case of supported Pd catalysts, Schüth and Wicke (27–29) found that for NO/CO ratios between 0.5 and 2 and at temperatures around 600 K, oscillations occurred. The reaction was followed using IR spectroscopy. Oscillations of isocyanate bands appeared to be in counterphase to the reaction rate oscillations. Small-amplitude oscillations of the CO$_a$ bands were in phase with the reaction rate. The authors concluded that the Pd surface was blocked by N$_a$ and reactivated by the desorption of N$_2$. The oscillations were also accompanied by large thermal effects; differences up to 70 K were measured. It was observed that the catalyst was neither largely uncovered nor covered mainly with oxygen. The observed decrease in the intensity of the CO$_a$ and NO$_a$ bands can only be attributed to the formation of other adsorbates. Pd–NCO species were not found by IR spectroscopy. Support–NCO bands, formed on the fast spill-over of –NCO from Pd to the support, were very intense. This led to the conclusion that the Pd surface was covered mainly with N$_a$ atoms (29).

The spectra of Pt/CeO$_x$/Al$_2$O$_3$ show bands of isocyanate on Pt at 2180 cm^{-1} and on the alumina support around 2240 cm^{-1}. The band at 2240 cm^{-1} may well have a contribution from isocyanate on ceria (21, 24, 25). The question is, Can isocyanate inhibit the reaction? The spectra of Pt/Al$_2$O$_3$ showed only bands of isocyanate on the support (around 2240 cm^{-1}). Since we assume that one model should account for the deactivation, the discrepancy in mass balance and the occurrence of oscillations, –NCO as inhibitor of platinum can be ruled out, because no isocyanate on Pt was observed for the Pt/Al$_2$O$_3$ catalysts. Tanaka *et al.* (33) found that it is difficult to form N layers on Pt single-crystal surfaces.

Platinum oxide. It is striking that the spectra of Pt/Al$_2$O$_3$ and Pt/CeO$_x$/Al$_2$O$_3$ showed a stable band at 2120 cm^{-1} at higher temperatures. Alikina *et al.* (38) ascribed a band at 2105–2110 cm^{-1} to cyanide, CN$^-$, species on Pt. Dictor (36) found a band in the region 2130–2150 cm^{-1}, on coadsorption of CO and NO, which could possibly arise from adsorbed cyanide. However, by giving HCN injections to the fresh catalyst, no bands appeared around 2140 cm^{-1}. Numerous other authors have ascribed the band at 2115 cm^{-1} to linearly bound CO to Pt^{2+} (39–43), which we think is far more likely, especially since the band around 2120 cm^{-1} was also found with CO/O$_2$ gas mixtures. Our results indicate that, although the mixture was net reducing, a band of adsorbed CO arose on oxidized Pt. This was also found by Hegedus *et al.* (41) for Pt/Al$_2$O$_3$ catalysts at

505°C in mixtures of CO, NO, and O$_2$. The feed stream was periodically switched between net reducing and net oxidizing. With IR spectroscopy it was found that at the high-frequency limit (net oxidizing), the surface was covered by an intermediate amount of CO and it was free of isocyanates. With a reducing gas mixture, large bands of isocyanate were detected and there was a band at 2120 cm^{-1}. They concluded that some of the infrared-active species served as a temporary catalyst poison, since the growth of the 2120 and 2250 cm^{-1} bands is slower than their decay, implying that at higher cycling frequencies the surface concentration responsible for these bands diminishes, which leads to an increase in NO and CO conversion. According to these authors, the major inhibitor is CO, even though they could not exclude isocyanate (41).

Lindstrom *et al.* (40) reported an intense 2120 cm^{-1} band as well as oscillations of this band with periods as long as 10 to 15 min when they examined Pt/Al$_2$O$_3$ in CO/O$_2$ reactions. After the catalyst was subjected to a 24-h treatment in 10% CO in air, only a very small 2120 cm^{-1} band was observed. They could not explain why it was that oxidation treatment eliminated or reduced the ability of the catalyst to form 2120 cm^{-1} species. They suspected that during the treatment the catalyst is sintered appreciably. Since inactive oxygen species are more readily formed on more highly dispersed catalysts, due to higher percentages of edges and steps where the O$_2$ dissociation occurs preferentially (43, 44), sintering of the catalyst may lead to a retarding or decreasing formation of such inactive oxygen species.

Barshad *et al.* (42) observed that CO adsorbed on platinum oxide is very stable and does not take part in the CO oxidation reaction to any appreciable extent. They studied CO oxidation over Pt/Al$_2$O$_3$ under transient conditions. The platinum oxide, covered with CO, did not become reduced at any appreciable rate at their reaction temperature of 140°C.

We have shown in Figs. 6j and k that the 2115 cm^{-1} band does not disappear on the introduction of oxygen to the sample at 400°C. Linearly bound CO on Pt, however, can be removed at room temperature from Pt/CeO$_x$/Al$_2$O$_3$, probably by the reaction of CO with O$_a$, as was shown in Figs. 7h to k.

That the inhibiting species are very strongly bound to Pt is also seen when the $T_{50\%}$ for a fresh catalyst is compared with that for a catalyst after oscillation/deactivation experiments, in a CO/O$_2$ reaction with a CO/O$_2$ ratio to 1 : 1. The temperature of 50% O$_2$ conversion of Pt/CeO$_x$/Al$_2$O$_3$ after oscillations is 100°C higher than for a freshly reduced Pt/CeO$_x$/Al$_2$O$_3$ catalyst! See Figs. 8 and 9.

When CO and NO were added to a prereduced Pt/CeO$_x$/Al$_2$O$_3$ catalyst in a stoichiometric ratio (Fig. 7), no 2115 cm^{-1} band was formed. The intensity of all the bands decreased after 10 min at 350°C, which indicated smooth progress of the reaction of CO with NO according to the

above-described reaction pathways. No inhibition seemed to occur.

Formation and decomposition of Pt oxide were suggested by Vayenas *et al.* (45, 46). Oscillatory phenomena observed during ethylene oxidation on polycrystalline Pt films in a CSTR were modeled by the assumption that PtO_x is unreactive toward ethylene. Two types of Pt adsorption sites exist for atomic oxygen. The first is dissociatively chemisorbed oxygen and the second produces surface Pt oxide, PtO_x. The oscillations were found to occur on the fuel-rich side only.

We believe that the formation and decomposition of Pt oxide, as was suggested by Vayenas *et al.* (45, 46), cannot account for all the effects that were observed by us. Infrared bands of CO bound to Pt oxide are seen for both the $Pt/CeO_x/Al_2O_3$ and Pt/Al_2O_3 catalysts, but only the $Pt/CeO_x/Al_2O_3$ catalyst shows oscillatory behavior. The 2115 cm^{-1} band remained intense at high temperatures for prolonged times and only treatments in oxygen for several minutes diminished the intensity of this band (Fig. 6k). Another argument against Pt oxide formation (STM model) as a sole explanation for oscillation and deactivation is given by the CO oxidation experiments, shown in Figs. 8 and 9. If the oscillation and deactivation are caused by the formation of Pt oxide, one would expect $T_{50\%}$ for the second measurement to be at least the same, or even higher, than the $T_{50\%}$ for the first measurement directly after the CO/NO reactions, because an oxidizing CO/O_2 gas mixture was used. However, it was observed that the $T_{50\%}$ of the second measurement was lower than that of the first. It seems that due to the reaction in an oxidizing CO/O_2 gas mixture, part of the inhibiting species had been removed.

If the inhibiting species is a Pt^{n+}–CO species, the oscillations on $Pt/CeO_x/Al_2O_3$ are caused by the slow removal of CO by the reaction with O_a generated by the dissociation of NO on CeO_x or by the lattice oxygen of CeO_x. Deactivation of Pt/Al_2O_3 is caused by the buildup of Pt^{n+}–CO species and the concomitant decrease in vacant Pt sites, needed for NO dissociation. If the band at 2115 cm^{-1} is ascribed to CO bound to oxidized Pt^{n+}, this CO of the Pt^{n+}–CO band is apparently strongly bound to the platinum oxide and unreactive up to 400°C in an oxidizing atmosphere. This leads to the same conclusion as drawn by Barshad *et al.* (42), namely, that the CO of the Pt^{n+}–CO band at 2115 cm^{-1} is strongly bound to the platinum oxide.

The assumption that a Pt^{n+}–CO species is the inhibiting species leaves some questions unanswered. One question is why Pt is so easily oxidized in a net reducing gas mixture. Are highly dispersed Pt catalysts more susceptible to oxidation due to the preferential O_2 dissociation on edges and steps, as was suggested by Sárkány and Gonzalez (47) and by Cant (44). Another point is that, in general, less electron backdonation into the antibonding orbital of CO, indicated by a higher wavenumber value for the CO band, results in less strongly bound CO molecules. The band at

2115 cm^{-1}, however, is stable up to 400°C, thus indicative of a strongly bound species.

CONCLUSIONS

Several models are presented and discussed to explain the observed behavior of $Pt/CeO_x/Al_2O_3$ and Pt/Al_2O_3 catalysts in CO/NO reactions with a CO : NO ratio of 3 : 1. The Pt/Al_2O_3 catalyst is being deactivated with time under the net reducing gas mixture at 400°C. The $Pt/CeO_x/Al_2O_3$ catalyst shows oscillations in reactant and product gases at 400°C. FT-IR spectra reveal the possible existence of an inhibiting, blocking species that could explain the observed phenomena. No isocyanate species is detected on Pt metal of the Pt/Al_2O_3 catalyst, in contrast to the $Pt/CeO_x/Al_2O_3$ catalyst, where the characteristic Pt–NCO band is found. Since we believe that the deactivation of Pt/Al_2O_3 and the oscillations over $Pt/CeO_x/Al_2O_3$ must be explained by one model, isocyanate as inhibitor is ruled out.

Formation and decomposition of platinum oxide as a sole explanation are also ruled out, because the Pt/Al_2O_3 catalyst is deactivated and does not show any oscillatory behavior. In addition, a second measurement in oxidizing CO/O_2 gas mixtures shows a lower $T_{50\%}$ than the first measurement, directly after the oscillating or deactivating reactions. The best candidate seems to be an inhibiting species with CO as a constituent. The adsorbed inhibitor is strongly bound to Pt and difficult to oxidize, as is shown by CO/O_2 reactions after the oscillation/deactivation experiments. The inhibiting species are slowly removed with oxygen, generated by the dissociation of NO on CeO_x or by the lattice oxygen of CeO_x. Since with the buildup of inhibiting species on Pt/Al_2O_3, the NO dissociation on Pt is hindered more and more, the Pt/Al_2O_3 slowly deactivates with time.

REFERENCES

1. Imbihl, R., *Prog. Surf. Sci.* **44**, 185 (1993).
2. Van Tol, M. F. H., Mergler, Y. J., Koutstaal, C. A., and Nieuwenhuys, B. E., *Nevac blad* **32**, 93 (1994).
3. Slinko, M. M., and Jaeger, N. I., *Stud. Surf. Sci. Catal.* 86 (1994).
4. Ertl, G., *Adv. Catal.* **37**, 213 (1990).
5. Regalbuto, J., and Wolf, E. E., *Chem. Eng. Commun.* **41**, 315 (1986).
6. Sant, R., and Wolf, E. E., *J. Catal.* **110**, 249 (1988).
7. Onken, H. U., and Wolf, E. E., *Chem. Eng. Sci.* **47**, 1659 (1992).
8. Kaul, D. J., and Wolf, E. E., *J. Catal.* **91**, 216 (1985).
9. Kaul, D. J., and Wolf, E. E., *Chem. Eng. Sci.* **41**, 1101 (1986).
10. Kellow, J. C., and Wolf, E. E., *Chem. Eng. Sci.* **45**, 2597 (1990).
11. Aldhoch, W., and Lintz, H. G., *Z. Phys. Chem. N.F.* **103**, 207 (1976).
12. Burrows, V. A., Sundaresan, S., Chabal, Y. J., and Christman, S. B., *Surf. Sci.* **180**, 110 (1987).
13. Sales, B. C., Turner, J. E., and Maple, M. B., *Surf. Sci.* **114**, 381 (1982).
14. Van Tol, M. F. H., Gielbert, A., and Nieuwenhuys, B. E., *Catal. Lett.* **16**, 297 (1992).
15. Van Tol, M. F. H., Gielbert, A., and Nieuwenhuys, B. E., *Appl. Surf. Sci.* **67**, 179 (1993).
16. Van Tol, M. F. H., Wouda, P. T., and Nieuwenhuys, B. E., *J. Vac. Sci. Technol. A* **12**, 2176 (1994).

17. Van Tol, M. F. H., Siera, J., Cobden, P. D., and Nieuwenhuys, B. E., *Surf. Sci.* **274**, 63 (1992).
18. Shelef, M., and Otto, K., *J. Catal.* **10**, 408 (1968).
19. Cho, B. K., Shanks, B. H., and Bailey, J. E., *J. Catal.* **115**, 486 (1989).
20. Cho, B. K., *J. Catal.* **131**, 74 (1991).
21. Solymosi, F., *J. Catal.* **54**, 336 (1978).
22. Solymosi, F., Bánsági, T., and Novák, E., *J. Catal.* **112**, 183 (1988).
23. Martinez-Arias, A., Soria, J., Conesa, J. C., Seoane, X. L., Arcoya, A., and Cataluna, R., *J. Chem. Soc. Faraday Trans.* **91**, 1679 (1995).
24. Pande, N. K., and Bell, A. T., *J. Catal.* **98**, 7 (1986).
25. Pande, N. K., and Bell, A. T., *Appl. Catal.* **20**, 109 (1986).
26. Serre, C., Garin, F., Belot, G., and Maire, G., *J. Catal.* **141**, 9 (1993).
27. Schüth, F., and Wicke, E., *Dech. Monogr.* **120**, 429 (1989).
28. Schüth, F., and Wicke, E., *Ber. Bunsenges. Phys. Chem.* **93**, 191 (1989).
29. Schüth, F., and Wicke, E., *Ber. Bunsenges. Phys. Chem.* **93**, 491 (1989).
30. Schwartz, J. M., and Schmidt, L. D., *J. Catal.* **140**, 424 (1993) and references therein.
31. Collins, N. A., Sundaresan, S., and Chabal, Y. J., *Surf. Sci.* **180**, 136 (1987).
32. Engel, T., and Ertl, G., *Adv. Catal.* **28**, 1 (1979).
33. Tanaka, K. I., Yamada, T., and Nieuwenhuys, B. E., *Surf. Sci.* **242**, 503 (1991).
34. Bijsterbos, J. W., thesis, University of Amsterdam, 1993.
35. Ukisu, Y., Sato, S., Abe, A., and Yoshida, K., *Appl. Catal. B* **2**, 147 (1993).
36. Dictor, R., *J. Catal.* **109**, 89 (1988).
37. Niiyama, H., Tanaka, M., Iida, H., and Echigoya, E., *Bull. Chem. Soc. Jpn.* **49**, 2047 (1976).
38. Alikina, G. M., Davydov, A. A., Sazonava, I. S., and Popovskii, V. V., *Kinet. Katal.* **27**, 875 (1985).
39. Herz, R. K., and Shinouskis, E. J., *Appl. Surf. Sci.* **19**, 373 (1984).
40. Lindstrom, T. H., and Tsotsis, T. T., *Surf. Sci.* **167**, L194 (1986).
41. Hegedus, L. L., Chang, C. C., McEwen, D. J., and Sloan, E. M., *Ind. Eng. Chem. Fundam.* **19**, 367 (1980).
42. Barshad, Y., Zhou, X., and Gulari, E., *J. Catal.* **94**, 128 (1985).
43. Summers, J. C., *J. Catal.* **57**, 380 (1979).
44. Cant, N. W., *J. Catal.* **74**, 411 (1982).
45. Vayenas, C. G., Georgakis, C., Michaels, J., and Tormo, J., *J. Catal.* **67**, 348 (1981).
46. Vayenas, C. G., Lee, B., and Michaels, J., *J. Catal.* **66**, 36 (1980).
47. Sarkany, J., and Gonzalez, R. D., *Appl. Catal.* **5**, 85 (1983).