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In Situ FTIR Study of the NO + CO Reaction on a Silica-Supported Platinum Catalyst at Atmospheric Pressure Using a New Pulse Technique

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The CO + NO on the Pt/SiO_2 reaction is studied using a new pulse technique. This method allows one to simultaneously follow the surface species and the gas phase composition evolutions at atmospheric pressure and high temperature (498 K in this case) with a time resolution of about 1 s. When CO is pulsed in a NO continuous flow on the Pt/SiO_2 catalyst, the NO reduction occurs mainly at the end of the pulse. The N_2 selectivity of the reduction increases with the CO amount in the pulse. We show that these results correspond to a NO dissociation mechanism: CO reduces the platinum surface; NO adsorbs and dissociates on reduced Pt sites with recombination into N_2 and N_2O. The NO dissociation itself is a fast step and the N_2 selectivity increases with the availability of dissociation sites.

Key Words: **time-resolved pulse study;** *in situ* **infrared; nitrogen oxide reduction; NO + CO; Pt/SiO_2; selectivity; NO dissociation.**

INTRODUCTION

Study of the NO_x reduction mechanism (particularly in oxygen excess (1)) is nowadays one of the leading subjects in catalysis due to its great environmental impact. CO has been observed (in the gas phase or by spectroscopic methods at the surface) as a hydrocarbon partial oxidation product during the NO_x selective catalytic reduction (SCR) on several types of catalysts and despite oxygen excess (1, 2). Platinum-based catalysts still are among the most promising despite their high N_2O selectivity. Our own studies on the $NO + C_3H_6 + O_2$ reaction on Pt/SiO_2 (2) showed the existence of adsorbed CO in a reduced platinum environment (despite a large O_2 excess in the gas phase). This led us to focus on the NO + CO/Pt–SiO_2 reaction.

Since the hydrocarbon SCR of NO_x still has no practical application, recent results show that it is of practical interest to work under transitory conditions, for example, by a pulsed addition of reductant instead of a steady stream (3). The hydrocarbon can be pulsed directly in the motor at the end of the combustion cycle, whereas its continuous addition necessitates the adduction of a new line. Reaction efficiency can also be increased in this way. This led us to focus on the reaction mechanism under the pulse condition, using hydrocarbon (2) or CO reductant (this paper).

Many authors have proposed NO + CO/Pt reaction mechanisms. Most of these propositions imply a dissociation of NO on platinum with N_2 and/or N_2O recombination, the remaining surface oxygen being used to oxidize CO into CO_2 (4–7). Note that the same type of mechanism has been proposed for NO_x reduction by hydrocarbons in oxygen excess (8, 9). The precise steps can vary from one author to another, and the following equations have been proposed.

$$\mathrm{CO} + * \rightarrow \mathrm{CO}* \quad (* \text{ represents a Pt vacant site})$$
$$\mathrm{NO} + * \rightarrow \mathrm{NO}*$$
$$\mathrm{NO}* + * \rightarrow \mathrm{N}* + \mathrm{O}*$$
$$2\,\mathrm{N}* \rightarrow \mathrm{N_2} + 2*$$
$$\mathrm{NO}* + \mathrm{N}* \rightarrow \mathrm{N_2O} + 2*$$
$$\mathrm{CO}* + \mathrm{O}* \rightarrow \mathrm{CO_2} + 2*$$
$$\mathrm{NO}* + \mathrm{N}* \rightarrow \mathrm{N_2} + \mathrm{O}* + *$$
$$\mathrm{N_2O\ (or\ N_2O}*) + \mathrm{CO}* \rightarrow \mathrm{N_2} + \mathrm{CO_2} + *$$

Many authors postulate that the rate-limiting step is the NO dissociation itself (4, 7). Some authors, however, propose other mechanisms. Kinetics experiments led Klein *et al.* (10) to propose a mechanism implying a direct NO + CO bimolecular reaction, including

$$\mathrm{NO}* + \mathrm{CO}* \rightarrow \mathrm{CO_2} + \mathrm{N}* + *.$$

Surface isocyanate species has been identified under reaction conditions by spectroscopic methods. They are located on platinum and/or on support. The support-located species actually form on platinum and then spill over the support. There is no general agreement on these species' possible role in the reaction. Propositions vary from reaction intermediates (11) to reactive sites poisons (12) or inhibitors (by decreasing the availability of platinum

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electrons) (4). Since these species are easily detectable by IR techniques, our method (consisting of observing the surface species with IR under reaction conditions) will be useful for evaluating site occupation and their reactivity under real conditions.

Despite the abundant literature on this subject, some points remain unclear, partly because of a lack of correlation between spectroscopic and reactivity results. In any case, very little has been written on the N_2/N_2O selectivity of this reaction.

Our study uses a new pulse technique (i.e., in the present case CO pulses in a continuous NO flow on the catalyst), allowing one to correlate surface and gas phase variations under transient conditions. This powerful new method allows one to monitor both qualitatively and quantitatively all the parameters of the reaction and eventually to distinguish between different steps within the pulse passage. To our knowledge this had never been reported before. The variations induced by the pulse allow one to discriminate between spectator and reactive surface species. The technique has been inspired by the possibility of pulsing the reductant at the end of the motor cycle of a diesel vehicle instead of adding it continuously into the exhaust gas flow, and a further paper will present its application with hydrocarbon in excess oxygen (2). The method can also be considered a variation of the temporal analysis of products technique, extended to catalytic surface analysis and to atmospheric pressure.

EXPERIMENTAL

(1) Preparation of the Catalyst

The catalyst was made by exchange in ammoniacal medium, using a $Pt(NH_3)_4Cl_2$ precursor and a commercial DEGUSSA Aerosil 200 (200 $m^2 \cdot g^{-1}$) support. The last treatment was a 2-h calcination at 773 K. X fluorescence titration gave a Pt content of 3.6 wt% and a Cl residual content under the detection limit (0.01 wt%). The metal dispersion, as measured by H_2/O_2 cycles, was 30%.

(2) Study Method

The reaction takes place in an IR reactor cell, already described in detail elsewhere (13). It allows the observation of adsorbed surface species IR bands simultaneous with the analysis of the gas products during a catalytic reaction under continuous flow conditions. As an alternative to the continuous feed, a reactant can be punctually added using an injection loop and then introducing a transient perturbation to the system. The injection loop is passed through by a He stream corresponding to one-tenth of the total reactive flow. The dead volumes are minimized in the whole system in order to allow time-resolved analysis. Figure 1 shows the shape of a pulse after it passes through the catalytic reactor. Its shape is quasi-gaussian with a small trail.

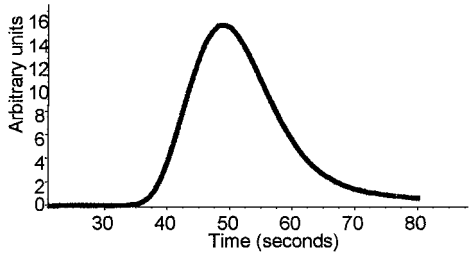

FIG. 1. Shape of a pulse.

Surface species spectra are obtained using a NICOLET Magna 750 IRTF spectrometer. All spectra of the adsorbed species were obtained by subtracting the spectrum of the activated wafer from the spectrum obtained after the introduction of the reactants. For the transient condition study, it is possible to collect up to one spectrum per 0.06 s. Such a time resolution is useless for the present study, in which one spectrum per 2 s was taken in order to ameliorate the signal/noise ratio.

Gas products are analyzed by FTIR (NICOLET Magna 750) in a gas microcell (multireflexion cell with an inner volume of 88 μl) and by mass spectrometry (Balzers TCP121). The analyses are made at the same time resolution as those of the surface. The origin of the time scale has been corrected to make it correspond to the surface analysis in the figures. Both IR and MS analysis techniques are complementary. IR allows one to quantify NO, CO, CO_2, NO_2, and N_2O concentrations. MS allows the analysis of the same gas plus the symmetrical molecules (N_2, O_2, H_2) and H_2O, but some masses correspond to the contributions of several molecules. This is particularly the case for mass 28, which corresponds mainly to N_2 and CO, but also to CO_2 (CO^+ fragment) and N_2O (N_2^+ fragment). Note also that mass 44 corresponds to the principal contributions of both CO_2 and N_2O. The precise quantification of the N_2 production (mass 28) is thus quite difficult. When needed, we have reproduced our experiments using ^{15}NO in order to separate the $^{15}N_2$ and $^{15}N_2O$ signals (in masses 30 and 46, respectively) from the major signals of CO and CO_2. The mass 30 signal has, however, been corrected from the $^{15}N_2O$ contribution for a better precision.

(3) Experimental Conditions

The catalytic sample was pressed into a 30-mg pellet (ca. 15 $mg \cdot cm^{-2}$). This corresponds to a surface Pt atom amount of ca. 1.66 μmol. The sample was pretreated at 498 K during 6 h under a He flow (25 $cm^3 \cdot min^{-1}$) and then under NO (1000 ppm) in a He flow at the same temperature. The aim was to obtain a NO-activated catalyst, neither fully oxidized nor fully reduced.

CO pulses of 10 or 20 μl (0.4 or 0.8 μmol, respectively, according to the perfect gas law) were punctually added to the NO (1000 ppm) in He continuous flow. The total

flow rate was maintained at 25 $cm^3 \cdot min^{-1}$ NTP (GHSV = 50,000 h^{-1}). The whole study was carried out at atmospheric pressure and 498 K.

RESULTS AND DISCUSSION

(1) Preliminary Attribution of Infrared Bands (CO and NO Adsorption on Pt)

The attributions of the platinum-adsorbed carbonyls are well known (14). We only observed linearly adsorbed CO/Pt, the wavenumbers of which depend on the platinum reduction state and the CO surface coverage. Adsorbed CO was observed in our case on oxidized platinum at about 2120 cm^{-1} (CO_{lin}/Pt_{ox}-oxidation degree of Pt: +II) and on reduced platinum below 2100 cm^{-1}. The classical wavenumber for CO_{lin}/Pt_{red} is 2050 cm^{-1} for an isolated vibrator and increases with surface coverage due to vibrational coupling.

Figure 2 shows the IR spectrum obtained by a continuous flow of NO (1000 ppm in He) on Pt/SiO_2 at 498 K. We first established that no significant NO adsorption occurred on the silica support. Each of the numerous IR bands obtained at 1540, 1632, 1721, 1797, 1833, 1933, and 1988 cm^{-1} then corresponds to coordinated species on platinum. The spectrum partly differs from those usually published, because most of the studies deal with monocrystalline reduced Pt, generally at ambient temperature and low pressure.

The band at about 1540 cm^{-1} has been attributed to a nitrate species on platinum (15). The band around 1632 cm^{-1} has been attributed either to bent (15–17) or to bridged nitrosyl (18, 19) on Pt. Studies on monocrystalline Pt (19, 20) have shown that the 1721-cm^{-1} band corresponds to the nitrosyl linearly adsorbed on Pt(111) microfacets. This band does not appear before the first CO pulse and must therefore correspond to a CO-assisted reconstruction of platinum. The linear adsorption is mentioned at higher wavenumbers on other faces and depends on the oxidation degree of the platinum. We then attribute the observed 1797-cm^{-1} band to nitrosyl linearly adsorbed on a reduced Pt (NO_{lin}/Pt_{red}) and that at 1833 cm^{-1} to an adsorption on oxidized Pt (NO_{lin}/Pt_{ox}).

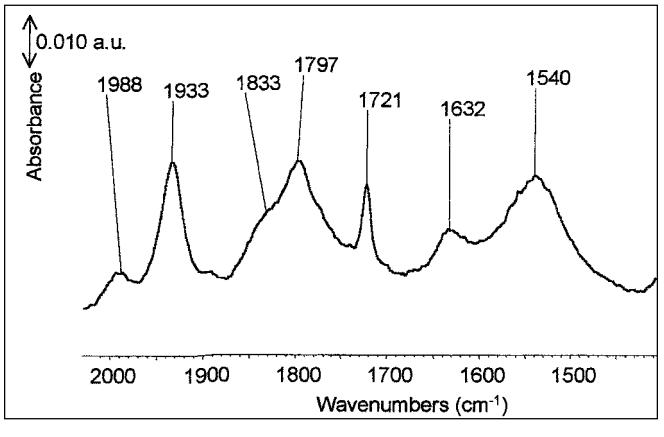

FIG. 2. IR spectrum of species arising from NO adsorption on Pt/SiO_2 at 498 K. Continuous flow of NO (1000 ppm) in He (25 ml $\cdot$ min^{-1}) between two CO pulses.

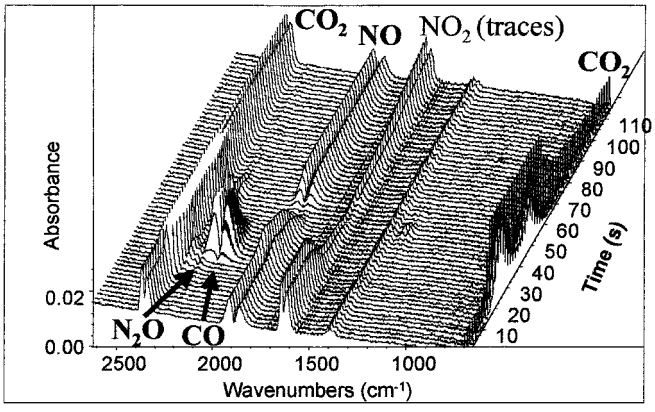

FIG. 3. IR spectra of the gas phase when pulsing 20 μl of CO in a 1000-ppm NO in He continuous flow on a Pt/SiO_2 catalyst; $T = 498$ K. One spectrum per 2 s.

The bands at 1933 (observed by De Jong *et al.* (18)) and at 1988 cm^{-1} (never observed to our knowledge) do not appear at ambient temperature. Their isotopic shifts using ^{15}NO are of 38 and 40 cm^{-1}, respectively, and correspond to those of the nitrosyl species. Their wavenumbers are too high to correspond to bridges or bent species. Their wavenumbers are higher than that of the gas NO molecule (1879 cm^{-1}): the species are of higher energy than NO (gas), indicating that their $2\pi^*$ antibonding bonds are less filled. These species are thus partly positively charged, but the wavenumbers are too low to correspond to nitrosonium (identified at 2133 cm^{-1} on ZSM5 (21)). We tentatively assign these two bands to NO linearly adsorbed on small oxidized Pt crystallites.

(2) Reduction of Flowing NO by a 20-μl Pulse of CO on Pt/SiO_2

Figure 3 shows the evolution of the gas phase when pulsing 20 μl of CO in a continuous flow of NO (1000 ppm) in He, presented as a succession of IR spectra as a function of time (1 spectrum per 2 s). Figure 4 presents the same analysis by mass spectrometry. Before the pulse, only NO (with traces of NO_2) and CO_2 (present in the optical bench, in constant concentration) are observed. Several other gases are detected during the pulse passage: N_2 (observable only by MS), N_2O, CO_2, and CO. The CO_2 production is clearly divided into two parts (two production maxima) which determine an easy subdivision of the pulse effects. The first CO_2 production peak is simultaneous to an *increase* of the NO gas phase concentration and the second to a NO consumption. No production of N_2 or N_2O (the two NO reduction products) occurs during the first CO_2 production, while the second corresponds to an important N_2 and N_2O

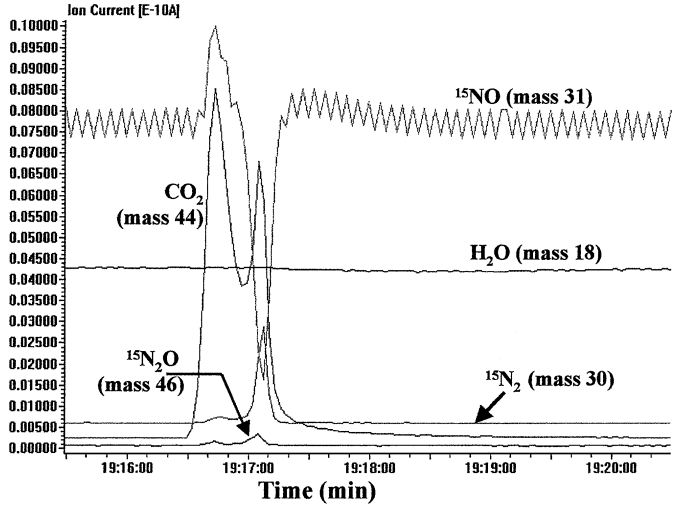

FIG. 4. MS analysis of the gas phase when pulsing 20 μl of CO in a 1000-ppm NO in He continuous flow on a Pt/SiO_2 catalyst; $T = 498$ K. ^{15}NO has been used in order to distinguish between N_2 and CO and N_2O and CO_2 in the MS quantification. Mass 28 (CO^+) is not shown here.

production. A CO peak (not shown on MS spectra) is observed at the end of the first CO_2 production only. This implies that the beginning of the CO pulse is totally consumed. The CO excess peak stops before the second CO_2 production maximum (which is simultaneous to the NO consumption/N_2 and N_2O production maxima).

Figure 5A shows the evolution of the surface species on the catalyst during the pulse (same time scale as in Fig. 3). Figure 5B details the IR bands present at the different steps of the pulse. Among the IR bands present before the pulse, we distinguish (from higher to lower wavenumbers) gas CO_2 in the optical bench (2349 cm^{-1}), present in constant concentration; CO on oxidized platinum (2122 cm^{-1}), only observed as a residue from a previous pulse; and the different forms of NO adsorption previously mentioned at 1988, 1933, 1833, 1797, 1721, 1632, and 1540 cm^{-1}. The simultaneous presence of the bands at 1797 and 1833 cm^{-1} indicates that the platinum is partly reduced and partly oxidized.

An important CO adsorption occurs during the pulse passage. Some adsorption takes place on oxidized platinum (2122 cm^{-1}), but the major band corresponds to CO linearly adsorbed on reduced platinum (CO_{lin}/Pt_{red}). Coupling effects between carbonyls cause its wavenumber to shift from 2050 (classical value at low CO coverage) to 2089 cm^{-1}. This CO_{lin}/Pt_{red} band totally disappears at the end of the pulse. The remaining CO_{lin}/Pt_{ox} band may correspond to a spectator species.

The nitrosyl bands under 1900 cm^{-1} strongly decrease at the beginning of the pulse. At the end of the pulse (when CO_{lin}/Pt_{red} disappears from the surface), they increase again up to an intensity higher than that initially shown and then slowly return to their initial levels. The higher wavenumbers nitrosyl bands (at 1933 and 1988 cm^{-1}) are not affected and then probably correspond to spectator species. The nitrate band at 1540 cm^{-1} partly disappears in the presence of CO and only slowly reconstitutes after the pulse. A very weak isocyanate band on platinum (at 2181 cm^{-1}) can be observed during the pulse. Its detection is difficult and we cannot determine precisely at which moment it disappears.

In order to correlate gas phase and surface information, we integrated the major IR bands identifying each species as a function of time at the same time scale (Fig. 6). Before the pulse, the Pt surface is occupied by nitrosyls and nitrates, as well as by adsorbed oxygen originating from the initial NO dissociation. This last species is not directly observable by our IR method, but the presence of the 2122- and 1833-cm^{-1} bands (CO_{lin}/Pt_{ox} and NO_{lin}/Pt_{ox}, respectively) is indirect proof of its existence.

When sending a CO pulse, two successive periods can be distinguished in its effects, as follows.

First period: Reduction of the Pt by CO. The diminution of the NO/Pt concentration at the beginning of the pulse does not correspond to a significant reduction of NO

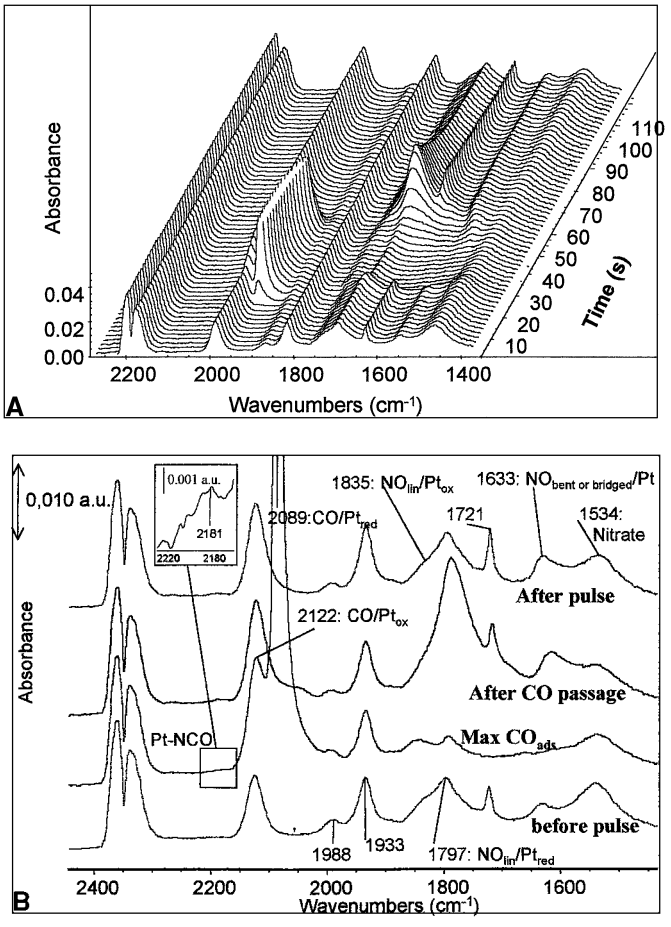

FIG. 5. IR spectra of the surface species when pulsing 20 μl of CO in a 1000-ppm NO in He continuous flow on a Pt/SiO_2 catalyst; $T = 498$ K. A: Waterfall of spectra, one spectrum per 2 s. B: Main steps of the pulse.

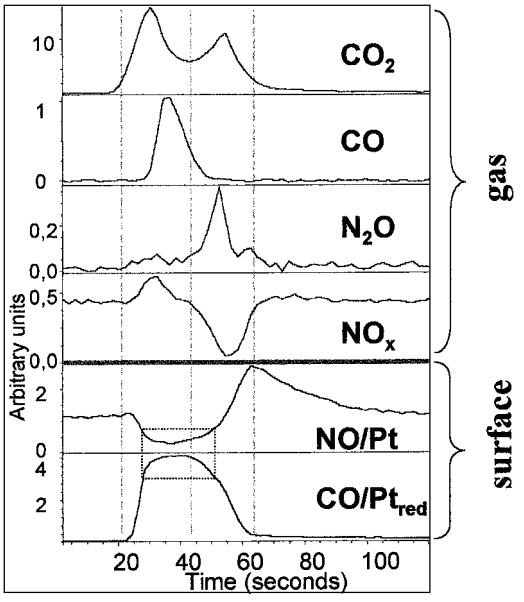

FIG. 6. Correlation between the surface species and the gas phase IR analysis when pulsing 20 μl of CO in a 1000-ppm NO in He continuous flow on a Pt/SiO$_2$ catalyst; $T = 498$ K.

(no significant production of N_2/N_2O), but to a desorption of nitrogen monoxide: the amount of observed gas NO increases during this period. The adsorbing CO displaces NO from the surface but does not react with it. The concomitant production of CO_2 can then only be justified by a reaction between CO and the initially adsorbed oxygen: CO reduces the platinum surface.

A saturation occurs at the end of this period. The CO_{lin}/Pt concentration does not increase any more, whereas a CO excess is present in the gas phase. The CO_2 production decreases because of a lack of adsorbed oxygen.

Second period: Reduction of NO. At the end of the pulse, CO progressively disappears from the surface, whereas NO reoccupies the Pt sites. The important NO consumption does not correspond only to this readsorption, but mainly to an important N_2/N_2O production (i.e., a NO_x reduction). CO_{lin}/Pt_{red} undergoes a total oxidation into CO_2, because no more CO is observed in the gas phase and no carboneous species remains on the surface (if we except the initial CO_{lin}/Pt_{ox} spectator species). This second CO_2 production corresponds to the N_2/N_2O formation, and NO is the only possible oxidant: CO_{lin}/Pt_{red} is the origin of NO reduction. We will thereafter discriminate whether this cause is direct or indirect.

At the end of the pulse, the NO/Pt concentration is higher than at the beginning. In fact, adsorbed nitrosyl species now occupy Pt sites occupied by other species before the pulse (O_{ads} or nitrates). The surface then slowly returns to its initial equilibrium.

How is the NO reduced? We could suppose a direct reaction between CO and NO on the surface, perhaps with an isocyanate intermediate. This species is actually present at very low concentration (it is detected at the sensibility limit) during both parts of the pulse, which is often the case for reactive species, quickly consumed after their formation. However, the absence of a reaction during the first part of the pulse, for NO/Pt and CO/Pt concentrations equivalent to those observed at the reduction maximum (see dotted rectangle in Fig. 6), invalidates this hypothesis. A reaction between gas CO or NO and, respectively, NO/Pt or CO/Pt is also to be excluded for the same reasons, as well as a direct reaction between NO and CO in the gas phase: those reactions would have taken place during the first period of the pulse as well as in the second.

This leads to the idea of an indirect reaction pathway. We propose a mechanism in which the crucial point is the availability of reduced Pt sites, on which adsorbed NO could dissociate. NO could then recombine into reduction products, according to the following equations:

$$NO* + * \rightarrow N* + O* \quad (* \text{ represents a Pt site}) \qquad [1]$$

$$N* + N* \rightarrow N_2 + 2* \qquad [2]$$

$$N* + NO* \rightarrow N_2O + 2*. \qquad [3]$$

The indirect role of CO is then to eliminate the adsorbed oxygen:

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

It is actually known (22) that O_{ads} cannot recombine and desorb as O_2 at the considered temperature (it begins to be possible around 673 K): the oxidation of CO is the only way to eliminate O_{ads} from the surface, which behaves as a poison for Pt_{red} dissociation sites (as is the case *before* the CO pulse).

We have seen that, in the first part of the pulse, CO eliminates the atomic oxygen initially adsorbed, thus reducing platinum sites. As long as a CO excess remains in the gas phase, this large amount of just-reduced Pt sites is immediately reoccupied by CO adsorbing from the gas phase, strongly limiting the possibility of NO dissociation. But at the end of the pulse this saturation phenomenon stops. A stock of CO_{lin}/Pt_{red} reductant has been constituted that can continuously reduce Pt sites. The dissociation reaction becomes then autocatalytic: each NO dissociation produces one O_{ads}, which liberates two dissociation sites by reacting with one CO_{ads} (desorption of N_2 or N_2O liberates two other sites). This justifies the very sharp N_2O peak. NO also continuously readsorbs on newly liberated Pt_{red} sites.

The dissociation mechanism is thus the only one able to explain the phenomena observed during the CO pulse. We must, however, confirm its existence: on an initially reduced Pt surface, this reaction should exist under our conditions in the absence of any adsorbed carboneous reductant. Note that NO decomposition on reduced platinum has already been shown by several authors (8, 23). Nevertheless,

checking this point under our particular conditions will allow us to get further information, particularly concerning N_2/N_2O selectivity.

(3) NO Dissociation on Prereduced Platinum

In this experiment, the catalyst has been prereduced by H_2 (10% in He) at 498 K during 4 h. We shall state that no N–H bond vibration is detected on the surface spectra and no NH_3 appears in the gas phase when pulsing NO on the catalyst. Therefore, no $NO + H_{ads}$ reaction can be suspected.

Figure 7 presents the MS gas phase analysis when pulsing 20 μl of NO 10 times on the catalyst. Only NO, N_2, and N_2O are detected.

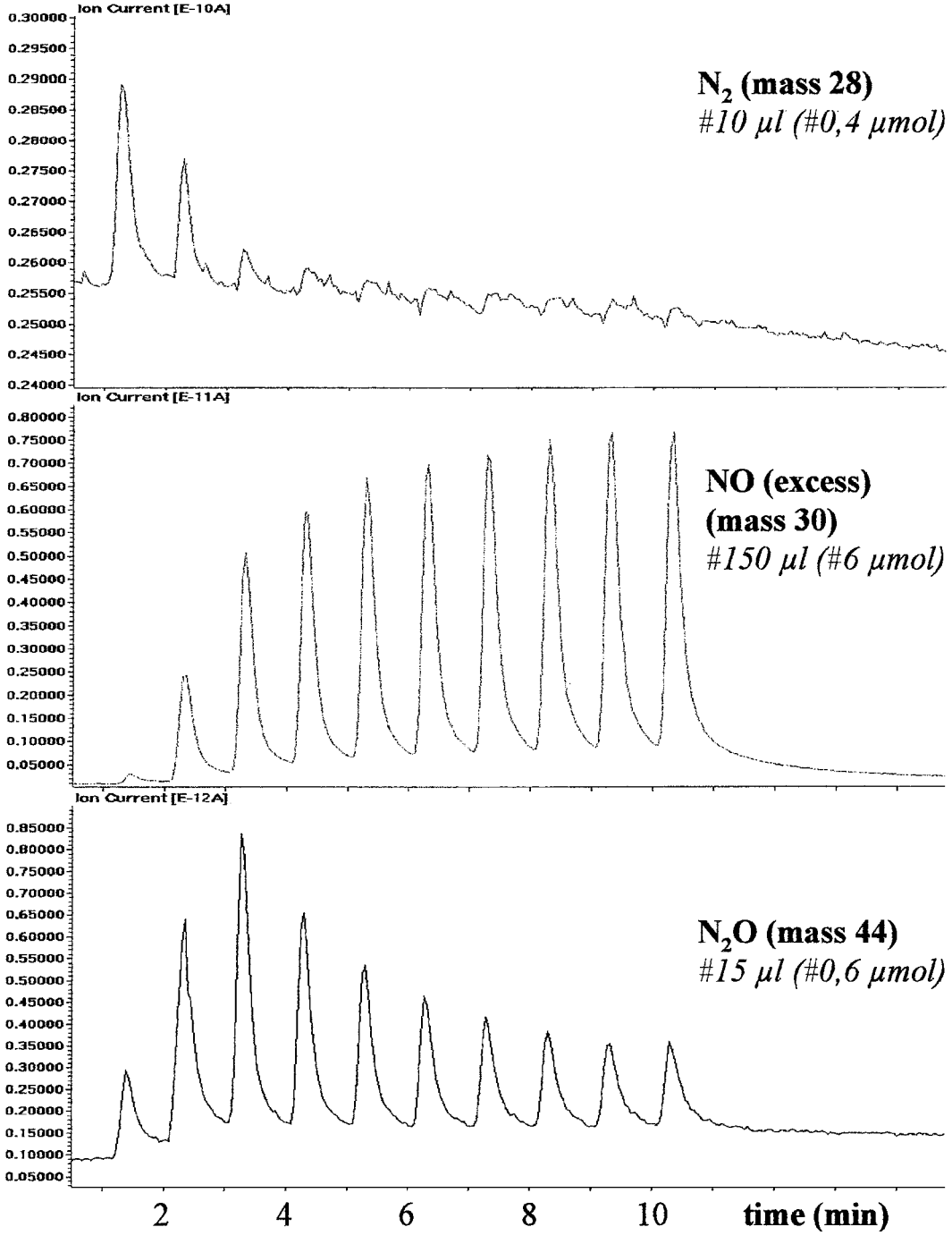

FIG. 7. MS analysis of the gas phase during NO pulses (10 times 20 μl) on a prereduced Pt/SiO_2 catalyst; $T = 498$ K, H_2 prereduction at 498 K. N_2O contributions to mass 28 (N_2) and 30 (NO) are negligible here; the NO contribution (due to fragment recombination within the mass spectrometer on mass 44 (N_2O)) is significant for the last pulses.

The first NO pulse is totally consumed and converted into N_2 (mainly) and N_2O (note that the mass 44 (N_2O) scale is much more dilated than that of mass 28 (N_2) in Fig. 7). Note that this pulse represents 0.8 μmol NO, which needs 1.6 μmol sites to fully dissociate. This approximately corresponds to the amount of available surface platinum sites.

NO conversion and N_2 selectivity decrease on each subsequent pulse. In the last pulses, the conversion is not significant any more. The nitrogen balance is verified, so no significant amount of NO stays adsorbed on the catalyst at the end of the experiment. IR spectra (not shown) confirm the presence of only a weak NO_{ads} band at this stage.

No O_2 production is detected by MS. There is a deficit on the oxygen balance of one O per N_2O produced (0.6 μmol) plus two O per N_2 produced ($2 * 0.4$ μmol). This implies that approximately 1.4 μmol O_{ads} stays on the Pt surface after the pulses. While the catalytic sample contains ca. 1.66 μmol surface Pt sites, we can conclude that the NO reduction has been progressively inhibited by the platinum oxidation.

This experiment demonstrates the reality of the NO dissociation mechanism, which is the only possible NO reduction pathway in the absence of a reductant. It is interesting to note that, when not limited by the availability of the dissociation sites, this mechanism is N_2 selective. This implies that the dissociation step [1] is shorter that the recombination into N_2O [3]. It also excludes a N_2O formation by direct reaction of a gaseous NO with an adsorbed nitrogen. Thus, despite the assertions of several authors (4, 7), the rate-limiting step of the reaction is *not* the NO dissociation itself.

N_2 selectivity decreases when some adsorbed NO in the neighborhood of adsorbed nitrogen finds no more Pt_{red} sites to dissociate. That is to say the more the surface platinum is reduced, the higher the N_2 selectivity by the dissociation mechanism. This gives us a simple way of confirming that NO reduction during a CO pulse occurs via a dissociation pathway, by comparing N_2 selectivity versus the amount of pulsed reductant.

(4) Comparison of the Reduction of Flowing NO by a 10- and a 20-μl Pulse of CO

When pulsing 10 μl (0.4 μmol) of CO in a 1000-ppm NO flow on the Pt/SiO_2 catalyst, the gas phase and the surface IR analysis results are qualitatively very similar to those obtained when pulsing 20 μl of CO. The major qualitative difference with the 20-μl (0.8 μmol) pulse described previously is that the 10-μl pulse is totally consumed (thus saturation is not attained). We can then consider that the platinum surface is reduced to a lesser extent by the 10-μl pulse, but that the explanations of the observed phenomena are identical. The intermediate low-activity period (between the two CO_2 production maxima) tends to disappear.

Table 1 compares quantitatively the N_2 and N_2O productions for both pulses. The N_2 production is higher and that of N_2O lower for the 20-μl pulse than for the 10-μl pulse. The global NO reduction is hardly higher for the 20-μl pulse: the greater amount of available reductant (both in the pulse and as CO_{lin}/Pt_{red}) corresponds much more to an increased N_2 selectivity than to an increased global NO reduction.

TABLE 1

N_2O/N_2 Production and N_2 Selectivity on CO Pulses

CO pulse (μmol)	N_2O production (μmol)	N_2 production (μmol)	$N_2O + N_2$ total (μmol)	Selectivity (N_2) (%)
0.4	0.018	0.021	0.039	53
0.8	0.014	0.027	0.041	66

This shows that the CO + NO reaction does not have an intrinsic selectivity, as could be the case for a direct reaction between adsorbed CO and NO molecules. On the contrary, the N_2 selectivity increases with the surface reduction capacity, as predicted by the dissociation mechanism. For this mechanism, the production of one N_2 needs the dissociation of two NO_{ads} (on reduced Pt sites), versus one NO_{ads} dissociation per one N_2O. The dissociation mechanism explains that N_2 selectivity increases in competition with global NO reduction.

CONCLUSION

The reduction of NO by CO on a silica-supported platinum catalyst has been studied by the addition of CO pulses in a continuous NO flow. This type of experiment shows that a direct reaction between CO and NO (adsorbed or not) must be rejected. CO actually reduces the platinum surface by reacting with the adsorbed oxygen and then allowing the renewal of reduced platinum sites. NO adsorbs and dissociates on these sites, and the resulting N_{ads} is recombined with NO_{ads} or N_{ads} to give N_2O or N_2, respectively. This mechanism is confirmed by the decrease in N_2 selectivity when the amount of pulsed CO is decreased. This evolution corresponds to that of the selectivity of the NO dissociation on an initially reduced platinum surface. In contrast with what has been previously published, the rate-limiting step is not the NO dissociation itself, which is intrinsically faster than the NO + N in N_2O recombination step. The reaction is actually limited by the availability of reduced Pt dissociation sites.

This study illustrates, using a quite easy example, the possibilities offered by a pulse technique, allowing the simultaneous qualitative and quantitative analysis and correlation of both surface species and gas phase evolutions during a transient-mode catalytic reaction. This method can be transposed to more complex reactions. The present paper actually is an introduction to a study of NO_x reduction by propene in oxygen excess on the same catalyst (2), in which

the existence of adsorbed CO in a reduced platinum environment is observed. It was important to first specify the possible role of this CO in the NO reduction reaction.

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