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Platinum catalyzed reduction of nitric oxide by n-butane in the presence of oxygen: role of the hydrocarbon

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Abstract

The mechanism of the catalytic reduction of nitric oxide by n-butane in an oxidizing atmosphere has been investigated at temperatures from 373 to 723 K. The reaction was carried out with a TAP (temporal analysis of products) reactor on a platinum sponge catalyst. When admitting pulses of NO alone on a reduced surface until reaching a steady surface coverage, the processes of NO reduction into N₂ and N₂O occur on time scales noticeable under TAP conditions according to the well accepted decomposition mechanism. When admitting oxygen and n-butane, the nitric oxide reduction is promoted: the N₂ yield reached 74% at 633 K compared to 6% only when admitting NO alone. The role of the hydrocarbon is not limited to the creation of free sites where NO can adsorb and dissociate. Carbon containing surface species formed during the hydrocarbon combustion increase the NO reduction by direct reaction between NO and these carbon containing species.

Keywords: Reduction; Nitric oxide; n-Butane; Platinum; Mechanism; Transient experiment

1. Introduction

The catalytic reduction of nitric oxide in the presence of an excess of oxygen, is an important goal in the context of the limitation of the NO emissions from diesel engines or power plants using fossil fuels. As an example Tabata et al. [1] reported, for a diesel engine operating continuously under typical conditions, that the exhaust gas contained around 15% O₂, 650 ppm NO_x, 195 ppm CO and 330 ppm total hydrocarbons (HC). The excess of oxygen is likely to induce the

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oxidation of CO into CO₂ and the total combustion of the hydrocarbon, leaving no reducing agent for the conversion of NO into N₂, NO being more likely converted into NO₂. It is known that carbon monoxide, which is a reducing agent under stoichiometric conditions as in the monolithic three-way reactor, is no more effective when oxygen is in excess [2–4]. Nevertheless, the NO reduction in an oxygen rich atmosphere was recently shown to be possible when using a hydrocarbon as reducing agent, as reviewed by Hamada [5] and Bethke et al. [6]. The hydrocarbon combustion induces the NO reduction at the condition that the light-off temperature is high enough to allow the NO activation but not too high to prevent from a too strong activity of O₂ for combustion and adsorption. The catalytic combustion of hydrocarbons was shown to occur via a Langmuir–Hinshelwood mechanism [7] where the oxygen and hydrocarbon adsorb on similar sites. The light-off temperature is related to the strength of adsorption of the hydrocarbon: the hydrocarbon should adsorb strongly enough on the catalyst surface to allow its oxidation by oxygen adatoms. But a too strong adsorption is detrimental to the combustion since the hydrocarbon is more difficult to oxidize and the oxygen adsorption is inhibited [8]. Thus, most commonly tested hydrocarbons for the NO reduction have been light alkanes and olefins. Among the tested catalysts, the supported platinum catalyst appeared to be one of the most promising systems because of its thermal and hydrothermal stability [9].

Oxygen, which inhibits the NO reduction when using CO as reducing agent, presents on the contrary a positive effect in the presence of the hydrocarbon. In the first case, NO decomposes on free sites left by the CO oxidation and the inhibiting factor in a rich oxygen atmosphere is proposed to be either the competitive adsorption between molecular oxygen and NO according to a Langmuir–Hinshelwood mechanism [2] or the atomic oxygen occupying sites required for the NO adsorption [3,4]. Burch et al. [10] namely observed that NO did not convert into N₂ on a completely oxidized supported platinum catalyst. But in the presence of the hydrocarbon, oxygen is involved in extra steps. Depending upon the proposed mechanism the positive effect of oxygen is then attributed to either the hydrocarbon activation [9,11–15] and/or the nitrogen monoxide activation [15] or the capacity of oxygen to prevent the catalyst poisoning by carbon deposition [10].

Two main mechanisms for the NO reduction by hydrocarbons on supported platinum catalysts are presented in the literature. One of them involves the formation of an intermediate activated hydrocarbon, proposed to be either of the form C_pH_qO_r [11–13] or a hydrocarbon fragment [10] or a partially oxidized carbonaceous radical [9,14]. The dinitrogen formation results from a direct reaction of this intermediate with either NO [11,12] or NO₂ issued from NO [15]. This first type will be referred to as the *carbon-assisted mechanism*. The other mechanism presented by Burch et al. [10,16] suggests that the role of the hydrocarbon is predominantly to create free surface sites by removal of oxygen

adatoms; NO can adsorb on these free sites and decompose, leading to N_2 by recombination of nitrogen adatoms. This catalytic behaviour is similar to the one admitted for CO on a three-way catalyst, when operating at high temperature [17,18]. The mechanism was referred to by Burch et al. [10] as the *nitrogen monoxide decomposition / oxygen clean-off mechanism*. In this case the better reducing capacity of the hydrocarbon compared to carbon monoxide, when oxygen is present in excess, was explained by the ability of the hydrocarbon to generate per molecule a larger amount of reduced platinum sites than carbon monoxide.

The aim of the present work is to precise the role of the hydrocarbon, by means of a transient kinetic study with a TAP (temporal analysis of product) reactor. n-Butane was chosen since alkanes constitute one of the numerous classes of components present in exhaust gases [8,19] and because its light-off temperature seemed suitable for the reaction. The reaction was investigated on a platinum sponge catalyst. The different adsorbed and desorbed species involved as a function of temperature are summarized in Table 1, although the desorption temperature may depend on the species surface coverage [20]. O_2 adsorbs molecularly until around 100 K and dissociatively above this temperature [21]. The associative desorption of oxygen adatoms is observed from about 450 K [17]; the oxygen surface coverage decreases then from 100% to about 40% at 700 K where it reaches a stable value. NO was shown to adsorb molecularly until about 420 K [20]. Above this temperature NO starts to dissociate into nitrogen and oxygen surface adatoms and the recombination of nitrogen adatoms leads to N_2 . For temperatures lower than 450 K the oxygen adatoms left on the surface after NO decomposition would ultimately completely cover the surface and likely inhibit the NO reduction, as explained previously. But for higher temperatures some oxygen desorption is expected and the inhibiting effect of oxygen on the NO decomposition might not be total. Therefore the present paper investigates the inhibiting effect of oxygen adatoms resulting from NO decomposition by first performing experiments in the absence of n-butane and oxygen. In a second step the effect of n-butane and oxygen is presented. A mechanism

Table 1

Adsorbed species (noted *) and desorbed molecules, when admitting O_2 or NO on a polycrystalline platinum surface under TAP conditions, as a function of temperature

T / K	100	330	420	450
O_2	O-O **	O *		O *, O_2
NO	N-O *	N-O *, NO	N-O *, N *, O *, N_2 , NO, O_2	

taking into account the observed phenomena is finally proposed. The goal of this study was to emphasize on the identity, reactivity and life time of each of the involved surface species; this was achieved by always activating nitric oxide separately from n-butane and oxygen.

2. Experimental

2.1. Materials

Polycrystalline platinum sponge supplied by Johnson Matthey, containing 99.9 mass% Pt was used. The sieve fraction was 250–350 μm . The krypton BET surface area of the fresh catalyst equalled $0.05 \text{ m}^2 \text{ g}^{-1}$. The used gases were Ar (99.9999%), NO (99.5%), C_4H_{10} (99.95%), N_2 (99.995%), H_2 (99.999%) and CO (99.997%) from Hoekloos, O_2 (99.995%) and CO_2 (99.999%) from Air products.

2.2. Equipment

The TAP reactor used in these experiments has been described in detail elsewhere [22]. A typical experiment consisted in admitting a pulse of a limited amount of reactants into a microreactor maintained under vacuum and containing the catalyst. The typical residence time of gases in the reactor was 100 ms. If not specified, the pulse intensity was kept lower than 10^{16} molecules per pulse to allow Knudsen diffusion conditions in the catalyst bed. This resulted in a maximum total pressure above the catalyst lower than 1000 Pa. The reactor outlet signals of reactants and products were measured with a quadrupole mass spectrometer as a function of time until a baseline was reached, typically after a few seconds. The shape of the outlet pulse was a function of the various processes occurring in the reactor and on the catalyst surface: Knudsen diffusion, adsorption, desorption and reaction. Argon introduced with a low percentage in all reacting mixtures gave the reference signal corresponding to diffusion only through the reactor.

2.3. Procedures

The catalyst loading was typically 700 mg, positioned between two quartz beds of the same sieve fraction. In order to obtain a stable surface area the catalyst was pretreated in situ at 973 K: it was first oxidized under a continuous flow of O_2/Ar 90/10 mol-% at 10^{-7} mol/s for 1 h, then left under vacuum for half an hour and finally treated under a continuous flow of H_2/Ar 90/10 mol-% at 10^{-7} mol/s for 1 h. The final surface area equalled $0.03 \text{ m}^2 \text{ g}^{-1}$, corresponding to a monolayer capacity of $3 \cdot 10^{17}$ platinum atoms. It remained

stable during the whole investigation. Each experiment was repeated on a reactor filled with quartz only. A thermocouple was inserted into the catalyst bed for temperature measurement. The investigated temperatures were between 373 and 723 K.

Three types of experiment were performed. The first one was referred to as a *pulse experiment* where the response to one NO/Ar pulse was recorded. The second type of experiment was referred to as an *alternating pulse experiment*. Two single pulses of two different mixtures were consecutively introduced, the first mixture being $C_4H_{10}/O_2/Ar$ and the second one NO/Ar. Concerning the first pulse it was verified experimentally that the difference in diffusion rates of the reactants were sufficiently small to consider simultaneous diffusion through the bed. The time interval between both pulses was 2 s in order to avoid signal overlapping, and the total acquisition time 3 s. The time interval was also varied from 0.7 to 10 s to evaluate the life time and reactivity of the adsorbed species formed during the first pulse and probed during the second pulse. During both pulse and alternating pulse experiments, the acquisition consisted in monitoring at the same time Ar and another gas. Ar used as an internal standard allowed to correct for the eventual pulse intensity fluctuations throughout the complete acquisition. The outlet responses on each mass unit were accumulated around 30 times and time-averaged in order to improve the signal to noise ratio. Pulsing was continued until reaching identical outlet signals, corresponding to steady surface coverages of the catalyst. This final situation was referred to as the steady-state. After a final smoothing of the outlet curves, conversions, yields and mass balances in carbon, oxygen and/or nitrogen were calculated. The mass balances were a second criterion to conclude if the steady-state was reached. The third type of experiment was referred to as a *multipulse experiment*, where consecutive pulses were recorded separately, without pulse averaging. In this case the surface coverage did vary from one pulse to the other and the experiment gave information about the evolution of the adsorption/reactivity of the gases with increasing number of pulses, as a function of the previous surface treatment. Only one mass unit could in this case be monitored. The first series of experiments of this type concerned: (1) 500 or 1000 multipulses of $C_4H_{10}/O_2/Ar$ and monitoring of CO_2 produced by the combustion, followed by (2) oxygen multipulses and monitoring of CO_2 , to titrate the eventual surface carbon containing species formed during the $C_4H_{10}/O_2/Ar$ multipulses. In the second series of experiments, multipulses of NO/Ar were inserted between steps (1) and (2) and the dinitrogen formation was recorded.

The NO/Ar mixture had the composition 90/10 mol-%. The $C_4H_{10}/O_2/Ar$ composition was mainly 15/75/10 mol-%, called rich mixture. It was slightly overstoichiometric in hydrocarbon since the stoichiometric mixture would contain 6.5 times more oxygen than n-butane. This constituted optimized conditions regarding the poor hydrocarbon sensitivity and the limitation in the pulse intensity to stay under Knudsen regime. The pulse intensities were such that the

molar ratio C_4H_{10}/NO during the alternating pulse experiments was near one. Some supplementary experiments were performed with a lean $C_4H_{10}/O_2/Ar$ mixture of composition 6/84/10 mol-%, slightly understoichiometric in hydrocarbon. The m/e values chosen for the analysis of the different gases were: 18 (H_2O), 28 (N_2), 28 (CO), 30 (NO), 32 (O_2), 40 (Ar), 43 (C_4H_{10}), 44 (CO_2), 44 (N_2O), 46 (NO_2). On each m/e the eventual contribution of fragments of other gases or impurities was subtracted. In the alternating pulse experiments CO_2 and N_2O (both of atomic mass unit 44) were differentiated by monitoring the fragments corresponding to m/e 12 and 14. CO and N_2 (both of atomic mass unit 28) were differentiated in the same way. Absolute calibration factors of reactants and products, i.e. allowing to transform the observed signals into outlet molar flow rates, were determined on a quartz bed, at each investigated temperature. The carbon and nitrogen balances were estimated with an error margin of 16%, taking into account the uncertainty on the calibration factor, the pulse integration and the correction for mass overlapping. The oxygen balance was estimated within an error margin of 20% only because of the higher uncertainty on the measurement of water.

3. Results and discussion

3.1. Blank experiments

The pulse experiment with the NO/Ar mixture on quartz led to a significant nitric oxide conversion around 9% at 723 K only. Dinitrogen was the only product. During the alternating pulse experiments with sequential $C_4H_{10}/O_2/Ar$ and NO/Ar pulses, no hydrocarbon combustion was noticed until 723 K, where the *n*-butane conversion equalled 11% in the case of the rich mixture. The NO conversion was also only significant at 723 K. During the multipulse experiments, performed at 633 K, no hydrocarbon conversion nor dinitrogen formation were observed.

3.2. *NO* reduction in the absence of *n*-butane and dioxygen

3.2.1. Activity

Pulse experiments were performed with the mixture NO/Ar on a reduced catalyst, at 553, 633 and 723 K. The amount of admitted molecules per single pulse was equivalent to either 5% (case A) or 60% (case B) of the monolayer capacity. In case A, N_2 was the only product whereas in case B, N_2 and N_2O were formed. Their yields obtained under steady-state are presented in Table 2. They clearly increased with temperature. With the low pulse intensity this steady-state was difficult to reach. NO strongly adsorbed on the free platinum surface sites, as indicated from the low surface area of the NO outlet pulse. But

Table 2

Yields of N_2 and N_2O under steady-state during pulse experiments with the mixture NO/Ar 90/10 mol-% as a function of temperature, for different amounts of NO molecules admitted per pulse

	<i>T</i> (K)		
	553	633	723
(A) NO admitted = 5% of the monolayer capacity			
Y (N_2), %	n.d.	6 ^a	37
(B) NO admitted = 60% of the monolayer capacity			
Y (N_2), %	0	2	7
Y (N_2O), %	0	2	4

^a The steady-state could not be reached.

n.d.: not determined.

NO desorption was occurring on the time scale of the pulse, as expected from Table 1. This was attested from the much broader NO outlet signal than the one of argon, as depicted in Fig. 1. As a consequence, an amount of NO more than necessary to cover a monolayer had to be admitted before N_2 could be detected and the steady-state was only obtained at 723 K; the lower the temperature, the broader the NO outlet pulse, due to a slower desorption, so that the NO outlet pulse became difficult to be exploited. When using the large pulse intensity, the steady-state was reached after a few tens of pulses. The amount of desorbed NO was in this case negligible compared to the amount of pulsed NO.

3.2.2. Reaction sequence

Only the temperature of 723 K offered a sufficient precision on the TAP curves to be kinetically exploited. Fig. 2 represents the output pulses of Ar, NO and N_2 at 723 K in case A, under steady-state. Ar and NO came out first and at

Fig. 1. Responses of Ar and NO as a function of time at 633 K during pulse experiments with NO/Ar. An amount of NO equivalent to 3.5 times the monolayer capacity was admitted prior to the present measurement. The amount of NO per pulse was equivalent to 5% of the monolayer capacity.

Fig. 2. Normalized responses of Ar ($\times 3.5$), NO ($\times 1$) and N_2 ($\times 2.6$) as a function of time at 723 K during pulse experiments with NO/Ar, after having reached a steady surface coverage. The amount of NO per pulse was equivalent to 5% of the monolayer capacity.

the same time, Ar being representative of diffusion only in the reactor. The N_2 output pulse was clearly delayed compared to NO and Ar, as also observed by Burch et al. [10]. In reference to the well known mechanism for NO decomposition, this is attributed to the time needed for NO adsorption, dissociation and nitrogen adatoms recombination according to steps (1) to (3), where species with * are adsorbed species and * free platinum sites. Concerning dinitrogen it was demonstrated that it desorbs immediately from the metallic surface under these reaction conditions [23].

The same sequence in the outlet pulses occurred in case B and the N_2O output pulse had an intermediate position between NO and N_2 . The experimental results are consistent with the idea that the rate-determining step at 723 K is the $NO*$ dissociation (step (2)). The fact that NO came out at the same time as Ar can then be explained by a fast molecular adsorption and desorption without dissociation. And the N_2O behaviour is then consistent with the involvement of a nitrogen adatom issued from $NO*$ dissociation, i.e. with a significant formation time, and a non dissociated $NO*$ molecule according to step (4).

3.2.3. Effect of oxygen surface coverage

The elementary step (1) assumes that free platinum sites exist on the surface under steady-state, even if the $NO*$ dissociation produces oxygen adatoms. A

titration of the oxygen adatoms present on the surface after NO pulsing was therefore performed; CO pulses were admitted 5 min after the end of the experiment and the CO_2 formation was recorded. The steady-state surface coverage of oxygen adatoms at 723 K was calculated to be 40%, a value similar to the surface coverage obtained when saturating the surface with dioxygen and determined in a previous study [17]. It can therefore be expected that the oxygen adatoms partially inhibited the NO reduction at this temperature. The oxygen titration at 633 K after pulsing NO until steady surface coverage led to an oxygen adatom coverage lower than 20%, whereas the oxygen adatom coverage after saturating the surface with dioxygen at the same temperature is 50% [17]. This leads to the conclusion that, at 633 K and under the present conditions, the lower N_2 yield could not be explained by the presence of oxygen adatoms, but rather by the lower temperature. Lower temperatures lead to lower rates for steps (2) and (3) in particular and thus to lower N_2 yields. As a corollary a higher degree of coverage by NO^* is expected at lower temperature.

3.2.4. Effect of pulse intensity

The decrease of NO conversion when the pulse intensity increases, viz. Table 2, cannot be explained by a difference in the oxygen adatoms degree of coverage since the latter was found to be identical in both cases. It can better be ascribed to the lower ratio of the amount of adsorption sites to the amount of molecules admitted. It follows from Table 2 that the high pulse intensity is more favourable to the formation of N_2O . This can be explained by the higher probability for NO^* to find a N^* adatom on an adjacent site than to find a free site for further adsorption and dissociation, as also suggested by Hirano et al. [24]. Fig. 3 illustrates the state of the surface during the pulse as a function of the pulse intensity.

3.3. NO reduction when using the rich mixture of *n*-butane and oxygen

3.3.1. Alternating pulse experiments

The catalytic activities for the hydrocarbon combustion and the NO reduction were measured over the 373–723 K temperature range by pulsing alternatively $\text{C}_4\text{H}_{10}/\text{O}_2/\text{Ar}$ and NO/Ar , with a 2-s time interval and a total acquisition time

Fig. 3. Influence of the surface coverage on the adsorbed species and desorbed molecules during the pulse experiment with NO/Ar , for an amount of admitted NO molecules per pulse equivalent to 5% (case A) or 60% (case B) of the monolayer capacity. * denotes a free platinum site.

Fig. 4. Conversions of oxygen and n-butane and yields in carbon oxides as a function of temperature during the $C_4H_{10}/O_2/Ar$ pulses as part of the alternating pulse experiments. (■) O_2 , (□) C_4H_{10} , (×) CO_2 , (+) CO .

of 3 s. The amount of NO admitted per pulse was equivalent to about 5% of the monolayer capacity (to be related to case A in Section 3.2). The oxygen and n-butane conversions as well as the yields in carbon oxides obtained during the first pulse are presented in Fig. 4 as a function of temperature. The combustion products were carbon monoxide at 373 K and mainly carbon dioxide and water at higher temperature. A complete oxygen conversion was observed already at 553 K, whereas the n-butane conversion still increased until 723 K where it reached 100%. This increase was due to an increase of the selectivity in carbon monoxide. The carbon balance was slightly lower than 100% between 373 and 633 K and went down to 67% at 723 K; between 373 and 633 K the error margin on the carbon balance did not allow to conclude about eventual carbon deposition but carbon deposition was definitely occurring at 723 K. This contributed also to the increase of the butane conversion still after complete conversion of oxygen. During the subsequent NO/Ar pulse a significant amount of dinitrogen was formed from 553 K on, which increased with temperature. No NO_2 or N_2O were detected. An important feature is that CO_2 formation was significant at 633 K, viz. Fig. 5, and even more pronounced at 723 K. The steady-state was not reached for temperatures lower than 633 K but the steady-state obtained at 633 K led to a dinitrogen yield of 74%. A series of experiments with time intervals between both pulses varying from 0.7 to 10 s showed that the time interval had no influence on the dinitrogen formation, as shown on Fig. 6.

From these experiments it is clear that nitric oxide conversion occurs in the temperature range of the n-butane combustion. Furthermore the dinitrogen yield is much higher than when pulsing NO alone: at 633 K the dinitrogen yield equalled 74% with prior admission of oxygen and n-butane and only around 6% with NO alone, viz. Table 2. This means that n-butane can be an efficient

Fig. 5. Responses of N_2 , CO and CO_2 formed during the alternating pulse experiments at 633 K. The first pulse was $C_4H_{10}/O_2/Ar$ and the second one NO/Ar , with a 2-s interval.

reducing agent of NO in the presence of oxygen. Carbon containing species are present on the surface, at least for temperatures higher than 553 K, and they have a longer life time than the duration of the pulse since they can be further oxidized by NO in a subsequent pulse of the latter. Two possibilities have then to be considered: the carbon containing species may react either with oxygen adatoms left after NO reduction on free surface sites, or directly with NO. The first case would imply that NO decomposes on the surface the same way as it does in the absence of n-butane/oxygen. The comparison of the dinitrogen outlet pulse during these experiments, and during NO activation in the absence of oxygen and n-butane, helps to clarify this point. It can be seen from Fig. 7 that the N_2 outlet pulse appears quicker in the first case than in the second one. It was already stated that N_2 desorbs immediately from the surface after

Fig. 6. Response of N_2 formed during the NO/Ar pulses as part of the alternating pulse experiments at 633 K, as a function of the time interval between the $C_4H_{10}/O_2/Ar$ and the NO/Ar pulses.

Fig. 7. Normalized responses as a function of time at 633 K, of (A) Ar ($\times 1$) and N₂ ($\times 7.3$) during pulse experiments with NO/Ar only, (B) Ar ($\times 4.3$) and N₂ ($\times 1$) during NO/Ar pulses as part of the alternating pulse experiments.

formation [23]. It can therefore be concluded that the difference in N₂ appearance results from a different pathway for N₂ formation, which is faster when carbonaceous species are present on the surface. So the role of the hydrocarbon is not only to create free surface sites available for the NO decomposition according to steps (1) to (3). The nitric oxide decomposition/oxygen clean-off mechanism does not predominantly occur under the present conditions. The present results indicate that the carbonaceous species are oxidized by direct reaction with NO, leading to N₂. Now, the fact that the dinitrogen yield is stable over at least 10 s after the withdrawal of the reactants hydrocarbon/oxygen means that the concentration of the active species involved in the reaction is constant over at least 10 s. This result rules out any direct reaction between NO and gaseous or weakly adsorbed hydrocarbon, since the concentrations of the latter decrease with time under vacuum. On the other hand it is totally consistent with the involvement of a strongly adsorbed carbon containing species and therefore consistent with the carbon-assisted mechanism, as described in the

Fig. 8. Amount of molecules detected during the multipulse experiment at 633 K as a function of the number of admitted C₄H₁₀/O₂/Ar pulses. □, CO₂ formed during the C₄H₁₀/O₂/Ar multipulses. ■, CO₂ formed during the surface titration with oxygen immediately after the C₄H₁₀/O₂/Ar multipulses. ▨, N₂ formed during the NO/Ar pulses admitted immediately after the C₄H₁₀/O₂/Ar multipulses.

introduction. This proposition is going to be further investigated in the next section.

3.3.2. Multipulse experiments

The objective of the multipulse experiment was to test the reactivity of NO with the surface carbon containing species. To obtain reasonable conversions of all reactants, the temperature of 633 K was chosen. After having admitted C₄H₁₀/O₂/Ar pulses, a titration with oxygen led to a significant carbon dioxide formation. This attested that carbon containing species were definitely left on the surface. The amount of CO₂ molecules formed during the C₄H₁₀/O₂/Ar pulses and during the subsequent titration are represented by the first and second bars respectively in Fig. 8. It can be observed that the CO₂ amount formed by the hydrocarbon combustion during 1000 pulses of C₄H₁₀/O₂/Ar is twice the amount during 500 pulses. It can therefore be concluded that the carbon species left on the surface do not deactivate the hydrocarbon combustion, at least during the first 1000 pulses. This suggests that a low amount of sites is concerned by this carbon deposition or that the carbon deposition occurs on sites which are not active for the combustion. The carbon dioxide issued from the titration by oxygen was equivalent to 30 and 60% of the monolayer capacity, after 500 and 1000 pulses, respectively. The large figure indicates that the ratio of deposited carbon over deactivated platinum site is much larger than one and the proportional effect suggests that the carbon deposition is not deactivated by the deposited carbon species.

When NO/Ar multipulses were admitted after C₄H₁₀/O₂/Ar, dinitrogen was detected after about 40 pulses, as depicted in Fig. 9. 40 pulses of NO/Ar correspond to only 10% of the monolayer capacity. The fast dinitrogen forma-

Fig. 9. Response of N_2 at 633 K as a function of time, during the first NO/Ar multipulses (1 pulse every 2 s), after having admitted 500 pulses of $\text{C}_4\text{H}_{10}/\text{O}_2/\text{Ar}$.

tion is in contrast with the results obtained in the absence of n-butane and oxygen, where no immediate N_2 formation was observed. The amount of formed N_2 molecules as a function of the number of previously admitted $\text{C}_4\text{H}_{10}/\text{O}_2/\text{Ar}$ pulses is represented by the third bar in Fig. 8. It can be seen that an increase in the number of previously admitted $\text{C}_4\text{H}_{10}/\text{O}_2/\text{Ar}$ pulses induced an increase in the amount of dinitrogen formed, whereas the amount of free platinum site per $\text{C}_4\text{H}_{10}/\text{O}_2/\text{Ar}$ pulse remains the same. Furthermore, the subsequent titration of the surface with oxygen did not lead to any carbon dioxide detection. This means that all the carbon containing species formed during the $\text{C}_4\text{H}_{10}/\text{O}_2/\text{Ar}$ pulses were already oxidized during the NO/Ar pulses. The most important conclusion is therefore that NO is able to oxidize carbon containing surface species formed during the hydrocarbon combustion, through a direct reaction between NO and these species.

3.4. NO reduction when using the lean mixture of n-butane and oxygen

Supplementary experiments were performed using a n-butane/oxygen mixture with an amount of oxygen significantly larger than necessary to burn all the hydrocarbon. Pulsing this mixture on platinum at 633 K led to a complete conversion of n-butane and to 66% oxygen conversion. The surface titration with oxygen after a preliminary treatment with the n-butane/oxygen mixture did not lead to any carbon dioxide formation. The hydrocarbon combustion is known to involve a Langmuir–Hinshelwood adsorption with further breaking of the weakest C–H bond [7]. The intermediate formation of carbon containing species on the surface is therefore expected. The experimental result shows that in the used lean conditions the carbon containing species formed during the

n-butane combustion were all further oxidized during the pulse by oxygen present in excess.

The NO activation after a preliminary treatment with the n-butane/oxygen mixture did not lead to any immediate dinitrogen formation. The result is similar to the one obtained when admitting NO alone, viz. Section 3.2. This demonstrates that the immediate N₂ formation during the NO pulses only occur in the presence of carbon species on the surface. It has to be emphasized that in real conditions oxygen, nitric oxide and hydrocarbon would be present at the same time, which is never the case in the present experiments. The key point of the reaction would then be that the intermediate carbonaceous species react with NO before being oxidized by oxygen.

4. Reaction mechanism

When admitting NO alone on the catalyst, the TAP technique allowed to confirm, by the sequence of the outlet pulses, the series of elementary steps already stated in the literature for the mechanism of NO reduction into N₂ on a clean surface, i.e. steps (1) to (3). When preliminary admitting n-butane and oxygen, it is clear that the predominant mechanism for dinitrogen formation is different, on the basis of the following observations: (i) dinitrogen formed under steady state showed a different pulse shape when n-butane and oxygen were used (viz. Fig. 7), (ii) a rather immediate dinitrogen formation was observed after the n-butane/oxygen treatment (viz. the multipulse experiments section), whereas its formation was not immediate on a reduced surface. This rules out the nitrogen monoxide decomposition/oxygen clean-off mechanism as the only mechanism, which assumes that the hydrocarbon liberates surface sites by consuming the adsorbed oxygen atoms. In this case, dinitrogen would be formed exactly through steps (1) to (3) and the kinetics of N₂ formation would be the same, with or without n-butane and oxygen. This study further revealed that the predominant route involves a carbon-assisted mechanism, for the following reasons: (i) during the alternating pulse experiments, carbon dioxide was generally formed at the same time as dinitrogen; (ii) NO was shown to be able to oxidize the carbon containing species left after n-butane combustion, by direct reaction with these intermediate species; this was concluded from the multipulse experiments; (iii) the immediate dinitrogen formation was not observed when the n-butane combustion left no carbon containing species on the surface; this was deduced from the experiments with the lean mixture. The involvement of carbon containing species is finally consistent with the relative stability of the involved intermediates, attested from the alternating pulse experiments. Therefore the following mechanism of NO reduction is proposed:

Oxygen activates dissociatively on the surface; the molecular oxygen sorption followed by dissociation, according to steps (5) and (6), was the only model to describe the dioxygen TAP response according to Huinink [17]. The hydrocarbon chemisorbs on free surface sites, with first breaking of the weakest C–H bond [7] (step (7)). I* denotes a carbon containing intermediate formed from n-butane after successive surface steps. NO reacts directly with this hydrocarbon intermediate to form dinitrogen (step (8)). The composition of I* is unknown. It could be a hydrocarbon fragment. Smirnov and Gorodetskii [25] namely showed that the reaction of NO with a small carbon cluster is possible and leads to N₂. Bamwenda et al. [13] observed by diffuse reflectance infra-red analysis C–H bands related to alkyl species, when performing the reaction on a Pt/Al₂O₃ catalyst with propene as reducing agent. But they proposed that the alkyl species is further oxidized into a species of the form C_pH_qO_r, which can react directly with NO. Possible surface intermediates are then cyanides and isocyanides, also detected by infra-red analyses. The present study does not allow to identify the involved intermediates. The above mechanism joins the one proposed by Ansell et al. [26] on Cu/ZSM-5 using propene as reducing agent. They concluded that NO₂ species formed from NO on copper sites reacted with adjacent coke, present on the support and active for the reaction. The role of oxygen was to activate NO by oxidizing it into NO₂. In the present case the positive effect of oxygen is more likely to prevent the catalyst from a complete deactivation by carbon deposition. This study shows that the presence of carbon containing species on the surface is nevertheless useful for the nitric oxide conversion.

These conclusions were drawn on the basis of experimental conditions which differed from the real conditions. Oxygen was not used in a large excess and the three reactants nitric oxide, oxygen and n-butane were never admitted simultaneously. This allowed the survival of carbonaceous species on the surface, which interaction with NO could be studied. In the present case they represented the real active intermediates. Under standard conditions, carbonaceous species are constantly generated during the combustion of the hydrocarbon, but their formation is only transient. The key point of the NO reduction is therefore believed to be the competition between oxygen and nitric oxide in their simultaneous oxidation of the carbon intermediate species. In this sense it is important to find out if the active carbonaceous species formed from a slightly rich mixture are still present and active under a lean mixture. The general characteristic of the reaction concerning the sharp maximum of NO conversion in the 200–350°C temperature range [5,9,10] is consistent with the proposed

mechanism when considering that at high temperature the reaction of oxygen with the carbonaceous species is the fastest. This characteristic was not observed under the present conditions. This has to be related to the alternative admission of oxygen and nitric oxide, which prevents from any competition, and the fact that carbonaceous species are left on the surface after the butane/oxygen pulse. This allows nitric oxide to be reduced at higher temperature than expected.

The mechanism holds for the hydrocarbon and catalyst used in this study, n-butane and platinum sponge. Other factors may have to be taken into account when using more complex catalysts. Hamada [5] pointed out the dependence of the catalytic activity on the presence of the support: alumina supported noble metal catalysts were active with propene and propane whereas non supported noble metal catalysts were only active with propene. Inaba et al. [27] attributed it to a cooperative effect between the metal and the support. Kintaichi et al. [28] reported a significant activity of the alumina itself, the presence of the noble metal allowing to lower the temperature for maximum NO conversion. The nature of the hydrocarbon is also important. On a same catalyst propane was reported to be less effective than propene [10,12]. Burch et al. [10] attributed it to a difference in the light-off temperature, the propane light-off temperature, higher than the one of propene, reaching a domain where the adsorption competition between dioxygen and nitric oxide was much in favour of dioxygen. This was on the assumption of the nitric oxide decomposition/oxygen clean-off mechanism. In the frame of the carbon-assisted mechanism the increase of light-off temperature may in a same way be more favourable to oxygen than nitric oxide in the reaction with the carbon containing species. Another possibility is that the carbon containing species formed from alkanes or olefins present a different reactivity towards NO.

5. Conclusions

Dinitrogen can be obtained on platinum by direct reaction of nitric oxide with carbon containing surface species, formed during n-butane combustion. Oxygen helps to prevent from complete poisoning of the surface but it competes with NO in the oxidation of the carbon containing intermediate. This competition is likely to be the limiting factor of the reaction. According to this mechanism the role of the carbon containing species is not limited to the removal of the oxygen adatoms from the platinum surface. Hence, the differences between several hydrocarbon and CO with respect to NO reduction should not only be discussed in terms of number of surface platinum atoms which are cleaned off but also in terms of selectivity for reaction with NO rather than with O₂. A better knowledge of the carbon containing intermediates may help to find a way to promote their formation and to orient the choice for the most suitable hydrocarbon.

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References

- [1] M. Tabata, H. Tsuchida, K. Miyamoto, T. Yoshinari, H. Yamazaki, H. Hamada, Y. Kintaichi, M. Sasaki and T. Ito, *Appl. Catal. B*, 6 (1995) 169.
- [2] M.J. Mummey and L.D. Schmidt, *Surf. Sci.*, 109 (1981) 29.
- [3] A. Amirmazmi, E. Benson and M. Boudart, *J. Catal.*, 30 (1973) 55.
- [4] A. Amirmazmi and M. Boudart, *J. Catal.*, 39 (1975) 383.
- [5] H. Hamada, *Catal. Today*, 22 (1994) 21.
- [6] K.A. Bethke, M.C. Kung, B. Yang, M. Shah, D. Alt, C. Li and H.H. Kung, *Catal. Today*, 26 (1995) 169.
- [7] Y.-F. Yu Yao, *Ind. Eng. Chem. Prod. Res. Dev.*, 19 (1980) 293.
- [8] G. Mabilon, D. Durand and Ph. Courty, *Stud. Surf. Sci. Catal.*, 96 (1995) 775.
- [9] A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno and H. Ohuchi, *Appl. Catal. B*, 2 (1993) 71.
- [10] R. Burch, P.J. Millington and A.P. Walker, *Appl. Catal. B*, 4 (1994) 65.
- [11] M. Sasaki, H. Hamada, Y. Kintaichi and T. Ito, *Catal. Lett.*, 15 (1992) 297.
- [12] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, *Appl. Catal.*, 75 (1991) L1.
- [13] G.R. Bamwenda, A. Ogata, A. Obuchi, J. Oi, K. Mizuno and J. Skrzypeck, *Appl. Catal. B*, 6 (1995) 311.
- [14] A. Obuchi, A. Ogata, K. Mizuno, A. Ohi, M. Nakamura and H. Ohuchi, *J. Chem. Soc., Chem. Commun.*, (1992) 247.
- [15] G. Zhang, T. Yamaguchi, H. Kawakami and T. Suzuki, *Appl. Catal. B*, 1 (1992) L15.
- [16] R. Burch and T.C. Watling, *Catal. Lett.*, 37 (1996) 51.
- [17] J.P. Huinink, Thesis, Eindhoven University of Technology, Eindhoven (1995).
- [18] B.A. Banse, D.T. Wickham and B.E. Koel, *J. Catal.*, 119 (1989) 238.
- [19] R. Impens, *Stud. Surf. Sci. Catal.*, 30 (1987) 11.
- [20] H. Miki, T. Nagase, T. Kioka, S. Sugai and K. Kawasaki, *Surf. Sci.*, 225 (1990) 1.
- [21] T. Engel and G. Ertl, in D.D. Elay, H. Pines and P.B. Weisz (Editors), *Advances in Catalysis*, Vol. 28, Academic Press, London, 1979, p. 1.
- [22] J.T. Gleaves, J.R. Ebner and T.C. Keuchler, *Catal. Rev.-Sci. Eng.*, 30 (1988) 49.
- [23] B.E. Nieuwenhuys, *Surf. Sci.*, 126 (1983) 307.
- [24] H. Hirano, T. Yamada, K.I. Tanaka, J. Siera, P. Cobden and B.E. Nieuwenhuys, *Surf. Sci.*, 262 (1992) 97.
- [25] M.Yu. Smirnov and V.V. Gorodetskii, *Catal. Lett.*, 19 (1993) 233.
- [26] G.P. Ansell, A.F. Diwell, S.E. Golunski, J.W. Hayes, R.R. Rajaram, T.J. Truex and A.P. Walker, *Appl. Catal. B*, 2 (1993) 81.
- [27] M. Inaba, Y. Kintaichi and H. Hamada, *Catal. Lett.*, 36 (1996) 223.
- [28] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki and T. Ito, *Catal. Lett.*, 6 (1990) 239.