A comparative study of the C_3H_6 + NO + O_2, C_3H_6 + O_2 and NO + O_2 reactions in excess oxygen over Na-modified Pt/γ-Al_2O_3 catalysts

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Abstract

The performance of 0.5 wt.% Pt (varying wt.% Na)/γ-Al_2O_3 catalysts in catalysing the C_3H_6 + NO + O_2, C_3H_6 + O_2 and NO + O_2 reactions under simulated lean-burn engine exhaust conditions, was investigated over a wide range of temperature (∼100–500 °C) and sodium loadings (0–4.2 wt.%). For the first two reactions, depending on the Na loading, both promoting and poisoning effects were obtained: optimal promotion was achieved at a sodium loading of 2.6 wt.%. On the other hand, NO + O_2 → NO_2 reaction was inhibited over the whole range of Na loadings used. In the promoting regime, Na widened the temperature window of the C_3H_6 + NO + O_2 reaction towards lower temperatures by ∼50 °C, accompanied by an enhancement in N_2-selectivity by ∼40 additional percentage points. For the C_3H_6 + O_2 reaction the propene *light-off* temperature and the temperature for 100% propene conversion decreased by 64 °C. Na loadings higher than the optimal loading caused a dramatic decrease in NO conversion over the whole temperature range in the case of C_3H_6 + NO + O_2 reaction, and a substantial decrease in hydrocarbon conversion for both reactions. Comparison of the C_3H_6 conversion profiles for these two reactions indicates significant inhibition of hydrocarbon oxidation by NO for all catalysts: nitrogen oxide increases the propene *light-off* temperature and the temperature of 100% C_3H_6 conversion by ∼80 °C. The promoting and poisoning effects of Na for all three reactions are understandable in terms of the influence of alkali modifier on the relative adsorption strengths of reactant species. The inhibition of hydrocarbon oxidation caused by NO and the propene-induced inhibition of NO_2 formation at low temperatures are understandable in terms of the competition of reaction intermediates for active surface sites.
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1. Introduction

Three-way catalytic converters (TWCs) have been highly successful in controlling NO_x, CO and hydrocarbon emissions from conventional engines that operate close to stoichiometric conditions [1]. However, they are no longer efficient in controlling NO_x emissions from lean-burn or diesel engines which operate at net-oxidising conditions thus contain large amounts of O_2 (∼5%). As a result,

significant efforts have been recently made for the selective catalytic reduction of NO (SCR) by means of hydrocarbons [2]. This potential process was first studied on Cu-ZSM-5 catalysts [3]. These studies showed that copper ion-exchanged zeolites exhibit high activity for the hydrocarbon-SCR of NO in the presence of excess oxygen. Large number of studies followed this pioneering work concerning the use of the same or other zeolite based catalysts [2,4–11]. However, this type of catalysts have hydrothermal stability problems [10], low activity in the presence of H_2O and SO_2 [4,10] in addition to undesirable selectivities towards CO [11].

Solutions for the hydrocarbon-SCR process have been also searched in conventional type supported catalysts such as Co/γ-Al$_2$O$_3$ [12], Ag/γ-Al$_2$O$_3$ [13–15] and primarily in supported Pt catalysts [16–30]. The latter catalysts show fairly high effectiveness on NO$_x$ reduction. However, they exhibit a considerably narrow temperature window of operation [16] at low temperatures in addition to significant selectivities towards N$_2$O [16–19], but they are not significantly affected by the presence of H$_2$O [29,30].

Recently we have shown that supported Pt-group metal catalysts promoted by electropositive promoters (alkalis or alkaline earths) exhibit important enhancements in both activity and selectivity towards N$_2$ during the reduction of NO by CO [31] or C$_3$H$_6$ [32–38]. Specifically, we showed that when Pt/γ-Al$_2$O$_3$ catalyst is promoted with the optimal amount of Na, K, Rb, Cs or Ba, the activity enhancements are up to two orders of magnitude during the NO + C$_3$H$_6$ reaction, accompanied with significant increases in N$_2$-selectivity (from ∼20% over the unpromoted Pt to values as high as 95% over the optimally promoted Pt) [33–37]. In addition, sodium promoted Pt/γ-Al$_2$O$_3$ catalysts were tested under simulated exhaust conditions at the stoichiometric point (1000 ppm NO/1067 ppm C$_3$H$_6$/7000 ppm CO/7800 ppm O$_2$) [38]. The results were very striking: significant decreases (ca. 100 °C) in the temperatures required for 100% conversion of NO, CO and C$_3$H$_6$ were observed, while the selectivity towards N$_2$ was improved from ∼75% over the unpromoted Pt to 100% over the optimally Na-promoted Pt [38]. Similar beneficial effects have been reported for Na-modified Pd/γ-Al$_2$O$_3$ catalysts operated under simulated TWC conditions [39], while Na addition on Rh catalysts was found to promote the NO reduction by propene in the absence of oxygen [40] and inhibit it under TWC conditions [41].

The described beneficial effects of electropositive promoters (alkalis and alkaline earths) on the NO reduction by hydrocarbons in the absence [32–37] or presence of oxygen [38–41] have been explained in detail. This explanation involves a promoter-induced increase in the strength of the metal (Pt, Pd or Rh)–electron-acceptor (NO, O or CO) bonds and a decrease in the strength of the metal–electron-donor (hydrocarbon) bonds, the former effect is accompanied by a weakening of the N–O bond on adsorbed NO molecules, thus facilitating NO dissociation during the de-NO$_x$ process [32–41]. Our electrochemical promotion (EP) studies involving in situ promotion by Na of Pt-film metal catalysts, over a series of similar reactions, such as NO + CO [42], NO + C$_3$H$_6$ [43] and CO + O$_2$ [44] were of great assistance in understanding the mode of action of electropositive promoters thus developing the above described model. Indeed, comparison of the achievements of the two methods of promotion (conventional and electrochemical) on a similar catalytic system showed many similarities [45]. As a result we concluded, among other things, that both methods are subjected to the same physicochemical rules [45].

A study of the H$_2$-SCR of NO in excess O$_2$ at low temperatures (ca. 50–200 °C) over Na and/or Mo-modified Pt catalysts was performed by Burch and Coleman [46]. They found promotional effects on NO reduction rate upon Na addition at low Na loadings (<1 wt.%) and very strong poisoning effects at much higher Na loadings (>5 wt.%). Na did not induce any significant effect in N$_2$-selectivity at this low temperature region [46]. However the authors found that Na and Mo-promoted Pt catalysts exhibit significantly enhanced NO reduction rate accompanied by remarkable increase in N$_2$-selectivity. Their results did not provide evidences that Na-addition enhances NO dissociation at this low temperature region, while the pronounced promotion in the case of Mo-modified Pt catalysts was attributed to the formation of an NH$_x$-type reaction intermediate adjacent to Mo oxide sites that can reduce NO to produce N$_2$.

Very recently, Vernoux et al. [47,48] extended the above studies of alkali promotion by investigating the NO reduction by propane and propene under conditions of excess O$_2$, applying both electrochemical promotion by Na, over Pt-film catalysts deposited on a Na$^+$ contacting solid electrolyte [47], and conventional promotion over Na-doped Pt/γ-Al$_2$O$_3$ catalysts [48]. They showed that substantial beneficial effects can be obtained by sodium promotion to this important process. Both methods of promotion offered similar effects on N$_2$-selectivity and conversion performance of Pt catalyst. Their results were explained in a similar manner to the ones given in our previous works.

In the present study the performance of electropositive alkali promoted catalysts, specifically Na-modified Pt/γ-Al$_2$O$_3$, is comparatively investigated for three reactions C$_3$H$_6$ + NO + O$_2$, C$_3$H$_6$ + O$_2$ and NO + O$_2$ at similar conditions of excess oxygen. The effects of temperature, Na loading and reactant contact time on products distribution and N$_2$-selectivity are studied.

2. Experimental methods

The catalyst was Pt highly dispersed over a γ-Al$_2$O$_3$ carrier, loaded with several amounts of Na promoter. The preparation procedure involved two subsequent impregnation steps as follows. Powder of γ-Al$_2$O$_3$ carrier (Alfa products, surface area ∼90 m^2 g^{-1}) was first impregnated in a solution of Pt(NH$_3$)$_2$(NO$_2$)$_2$ (Alfa products) with appropriate concentration in order to yield 0.5 wt.% Pt metal loading. After drying in air for 12 h at 110 °C, but before thermal decomposition of the active metal precursor, batches of this sample were impregnated with solutions containing various concentrations of NaNO$_3$. The solution concentrations were appropriately chosen in order to yield a range of Na loadings from 0 to ∼5 wt.%. The suspensions were initially dried in air at 80 °C and then overnight at 110 °C. The resulting samples were heated for 1 h in flowing He (100 cm^3 min^{-1}) at 400 °C, followed by H$_2$ reduction for 1 h at 400 °C in a hydrogen flow of 100 cm^3 min^{-1}.

Table 1

Properties[a] of the 0.5 wt.% Pt/γ-Al$_2$O$_3$ catalysts with different loadings of Na promoter, and total flowrates used (during acquisition of the conversion performance experiments) in order to keep the *effective contact time* of the reactant (NO or C$_3$H$_6$) constant and equal to 4 s for all catalysts when catalyst loading of the reactor was 70 mg

Catalyst code	Na loading (wt.%)	H$_2$ uptake, V_{H_2} (cm^3 STP/g$_{cat}$)	Dispersion (%)	Total flowrate for 4 s reactant contact time (cm^3/s)
C1	0.0	0.100	34.8	3.50
C2	1.6	0.060	20.9	2.10
C3	2.6	0.030	10.5	1.04
C4	4.2	0.025	8.7	0.867

[a] All the above surface characterization measurements refer to catalysts treated for 2 days at high temperature reaction conditions (550 °C; 1000 ppm NO/1000 ppm C$_3$H$_6$ /5% O$_2$).

Four Pt(Na)/γ-Al$_2$O$_3$ catalyst samples were produced (catalysts C1–C4, Table 1).

Before taking measurements, the catalysts were operated for 1 day in air and for 2 days in a reactive gas mixture, 1000 ppm NO/1000 ppm C$_3$H$_6$/5% O$_2$ at 550 °C in order to ensure stable operation (i.e., metal crystallite stabilization resulting from reaction or thermal sintering). After this pretreatment catalysts were characterized in respect to the exposed metallic area and thus metal dispersion by selective chemisorption of H$_2$ at 25 °C. Measurements for the determination of catalyst dispersions are listed in Table 1. Since these were taken after the above pretreatment, dispersion values can be considered stable during the acquisition of the catalytic performance data.

Catalytic performance experiments were carried out in a fixed bed, single pass, plug flow reactor, consisting of a 4 mm internal diameter quartz tube. The catalyst bed was held between plugs of quartz wool and a K-thermocouple was located in the center of the bed. Catalyst loadings were typically 70 mg (grain size 180–250 μm).

Air Liquide certified gas mixtures of 10% C$_3$H$_6$ in He, 7.83% NO in He and 20.7% O$_2$ in He were used. These were further diluted in ultrapure He (99.999%) and supplied to the reactor at 1 bar. Reactant gases were fed to the reactor through independent mass flow controllers (MKS type 247) to give a gas feed consisting of 1000 ppm NO/1000 ppm C$_3$H$_6$/5% O$_2$ with the balance He while investigating the C$_3$H$_6$ + NO + O$_2$ reaction, and 1000 ppm C$_3$H$_6$/5% O$_2$ or 1000 ppm NO/5% O$_2$ while investigating C$_3$H$_6$ + O$_2$ or NO + O$_2$ reaction, respectively.

During the experiments where the catalytic performance was examined regarding the conversions of the reactants versus temperature, the total flow rate used for each catalytic sample, was appropriately chosen to produce the same NO (or propene) *contact time* [31,33] of 4 s. Since the catalysts did not have identical dispersions (Table 1), the effective contact time of the reactant is the key parameter that should be kept constant in order to obtain a rational comparison of their relative merits. Effective contact time is defined as (surface Pt atoms)/(reactant molecules/s) [31,33]. In the

present case, a 4 s effective contact time required the total flow rates listed in Table 1 for each of the C1–C4 catalysts.

The reactor inlet and outflow were analysed using a Thermo Environmental Instr., 42C chemiluminescence NO$_x$ analyser (for NO and NO$_x$ = NO + NO$_2$ analysis) and an on-line Shimatzu 14B gas chromatograph with TCD detector. The chromatographic separation of N$_2$ and O$_2$ was performed in a molecular sieve 5A column while CO$_2$, N$_2$O and C$_3$H$_6$ were separated in a Porapak-N column, both columns operated at 80 °C. Since at low temperatures NO$_x$ can be accumulated to form sodium nitrate/nitrite on Na-doped Pt catalysts, attention was taken in order to ensure steady state before all the measurements. At lower temperatures (<200 °C) the time required to reach steady state was often more than 30 min. The total NO conversion calculated on the basis of NO conversion to N$_2$, N$_2$O and NO$_2$ products was found to close well, within 2%, with the difference [NO]^{in} − [NO]^{out} of the reactor inlet and outlet NO concentrations. This demonstrates a good closing of nitrogen balance.

3. Results

3.1. The C$_3$H$_6$ + NO + O$_2$ reaction

Fig. 1 shows the effect of catalyst's temperature on C$_3$H$_6$ (a) and total NO (b) conversion for the C$_3$H$_6$ + NO + O$_2$ reaction over Pt(Na)/γ-Al$_2$O$_3$ catalysts loaded with different amounts of sodium. The Na-free catalyst (C1) attains 100% propene conversion at 307 °C (Fig. 1a). However, Na-dosed catalysts C2 and C3 with 1.6 and 2.6 wt.% Na loading, respectively, exhibit profiles shifted at significantly lower temperatures. In particular, catalyst C3 (2.6 wt.% Na) offers the best hydrocarbon conversion achieving 100% C$_3$H$_6$ conversion at 250 °C (i.e., 57 °C lower than that of the Na-free catalyst C1). This beneficial effect of Na is not monotonic. Fig. 1a shows that further increase in sodium content of the catalyst (catalyst C4, 4.2 wt.% Na) causes a significant inhibition of the hydrocarbon conversion, shifting the temperature for 100% propene conversion to values higher than 500 °C.

The corresponding total conversion of NO is depicted in Fig. 1b. It is obvious that the Na-dosed catalysts C2 and C3, with 1.6 and 2.6 wt.% Na loadings, respectively, exhibit total NO conversion profiles shifted to about 60 °C lower temperatures in comparison to the Na-free case. It is also obvious that a significant widening of the NO conversion window is achieved by these two catalysts. Furthermore, increasing Na content of the catalyst causes a systematic decrease of the maximum achievable total NO conversion. For catalyst C4 which has the highest Na loading (4.2 wt.%) the NO conversion is almost fully suppressed.

For better understanding of the pattern of total NO conversion behaviour, Fig. 2 is constructed to analyse the various products obtained, i.e., N$_2$, N$_2$O, and NO$_2$ and
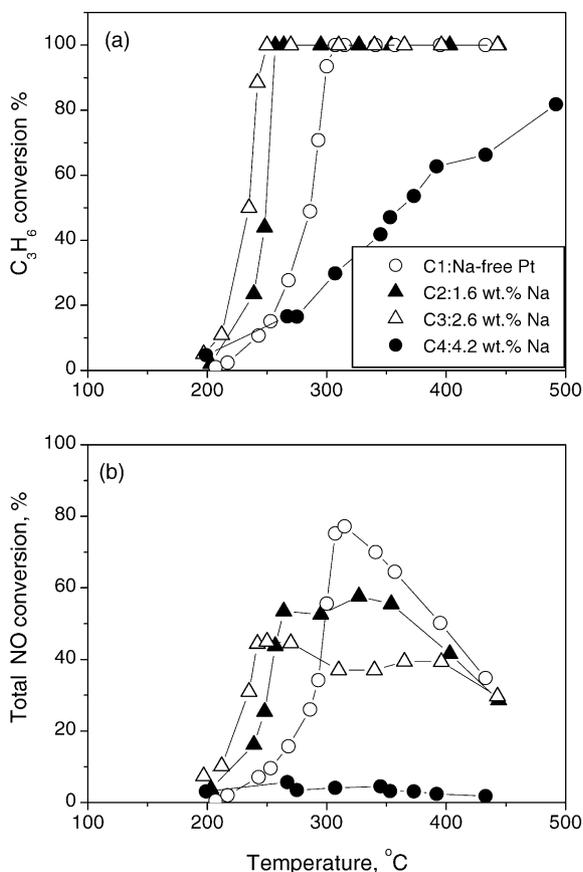
Fig. 1. $C_3H_6 + NO + O_2$ reaction. The effect of temperature on the conversion of C_3H_6 (a) and total conversion of NO (b) for the four catalysts in Table 1 with different Na loadings for constant inlet gas composition of 1000 ppm (v) NO, 1000 ppm (v) C_3H_6, 5% O_2. Reactant *contact time* is kept constant at 4 s. Catalyst weight 70 mg. Calculations: $X_i = \{([i]^{in} - [i]^{out})/[i]^{in}\} \times 100$, $i = C_3H_6$ or NO, where $[i]^{in}$ or $[i]^{out}$ is the inlet or outlet gas stream concentration of i species.

the corresponding N_2-selectivity related to the consumption of NO. As shown in Fig. 2a, the production of N_2 on the Na-free catalyst reaches a maximum of 17.5% at 293 °C. At this temperature the corresponding propene conversion is about 50%. For the same catalyst, NO conversion to N_2O exhibits similar ''volcano'' behaviour (Fig. 2b) with a maximum of 23.9% which is sited at a slightly higher temperature (307 °C) than that corresponding to maximum N_2 production. At this temperature propene conversion becomes 100% (Fig. 1a), NO_2 production begins and then is sharply increased by increasing temperature, passing also through a maximum (Fig. 2c). The above described behaviour of the Na-free Pt catalyst is similar to that reported in the literature [2,18,27,48].

However, significant differences in the distribution of N-containing products are observed due to Na addition to the catalyst (Fig. 2a–d), as summarized into the following main points:

(1) N_2 production characteristics (Fig. 2a): N_2 production is remarkably enhanced and at the same time, both high

and low-temperature ends of N_2-profiles are shifted to higher and lower temperatures, respectively, upon increasing Na content of the catalyst up to its optimal loading of 2.6 wt.%. Thus a widening—preferably towards lower temperatures—in the N_2 production window is achieved. The superior behaviour of the optimally promoted catalyst C3 (2.6 wt.% Na) offers a maximum NO conversion to N_2 of 28.9% at 242 °C (i.e., 11.4% higher and at 51 °C lower temperature in comparison to the Na-free catalyst). In contrast, catalyst C4 with the higher Na loading (over-promoted catalyst) shows a significantly suppressed N_2 production that reaches almost zero values.

(2) N_2O production characteristics (Fig. 2b): N_2O production is suppressed and at the same time, the low-temperature ends of N_2O-profiles are shifted to lower temperatures when increasing Na content of the catalyst up to its optimal loading of 2.6 wt.%. Similar to N_2 production behaviour, N_2O production is almost completely suppressed for the over-promoted catalyst (C4, 4.2 wt.% Na).

(3) NO_2 production characteristics (Fig. 2c): NO_2 production shows a systematic suppression upon increasing Na content of the catalyst in the whole temperature range investigated. In addition, maxima of NO_2 profiles are shifted towards higher temperatures.

(4) N_2-selectivity characteristics (Fig. 2d): the above described influence of the Na content of the catalyst on the N-containing product distribution causes remarkable effects on N_2-selectivity versus temperature, as shown in Fig. 2d. N_2-selectivity is systematically enhanced as a function of Na loading in the whole temperature range. This enhancement is more pronounced at elevated temperatures where the selectivity values of the optimally promoted catalyst C3 are, in principle, ~40 percentage units higher than those of the Na-free catalyst.

Fig. 3 shows the effect of the effective reactant (NO or C_3H_6) contact time, τ, on the $C_3H_6 + NO + O_2$ reaction output characteristics for one of the catalysts of Table 1 (C2, 1.6 wt.% Na). The temperature of the catalytic bed is kept constant at 257 °C. At low contact times, which correspond to values below that required to achieve 100% hydrocarbon conversion, the hydrocarbon conversion, the total NO conversion and the conversion of NO to N_2 and N_2O products increase upon increasing τ (Fig. 3). Moreover, NO_2 production is zero and N_2-selectivity gradually decreases after increasing the contact time, from a value of 70.3% at $\tau = 1.3$ s up to a value of 50.5% at $\tau = 4$ s. After 100% propene conversion is reached, further increase in contact time has no effect on the propene consumption (which remains at 100%), while the conversion of NO to N_2 and the N_2-selectivity are slightly increased in this region. The usefulness of *effective reactant contact time* for straightforward quantitative comparison of the conversion performance of different catalysts has been discussed elsewhere [31,33].
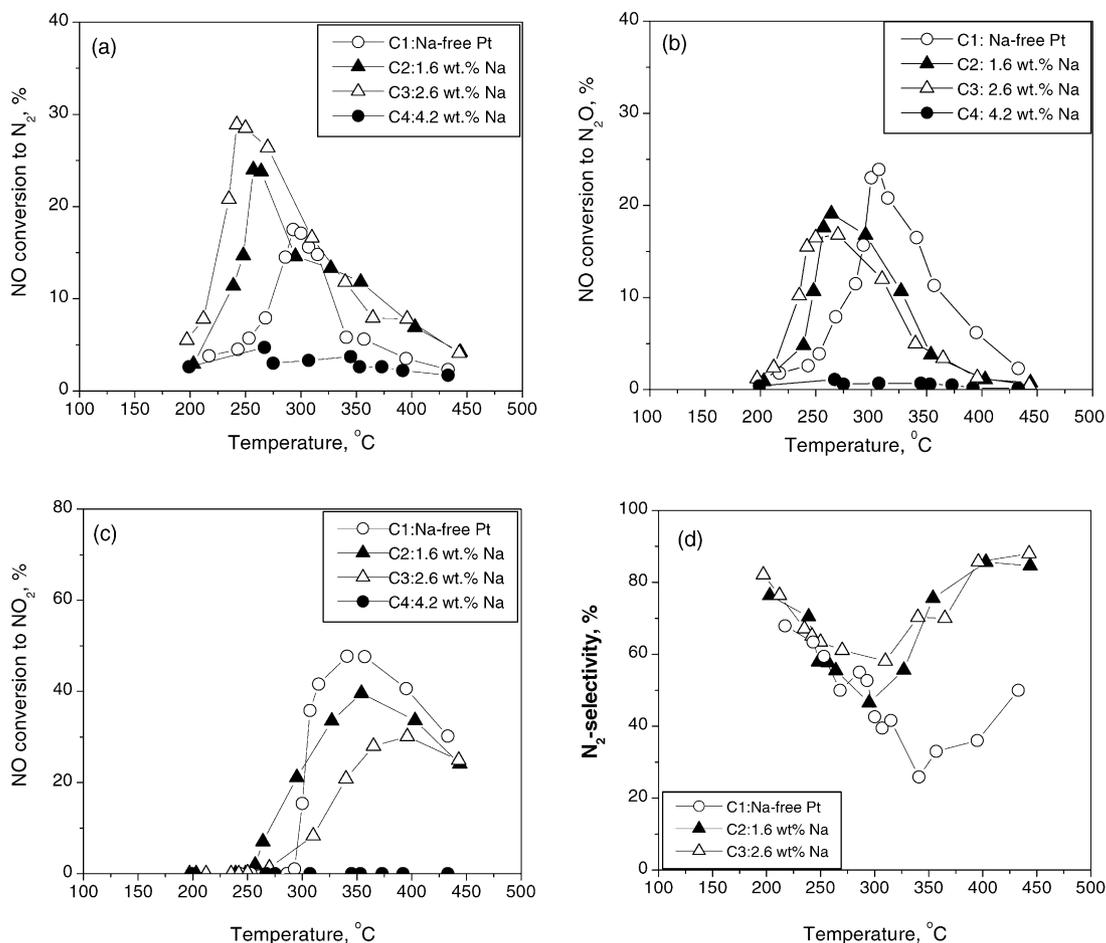
Fig. 2. $C_3H_6 + NO + O_2$ reaction. The effect of temperature on the conversion of NO to various N-containing products and the corresponding N_2-selectivity: (a) NO conversion to N_2; (b) NO conversion to N_2O; (c) NO conversion to NO_2; (d) N_2-selectivity. Conditions as in Fig. 1. Calculations: NO conversion to N_2 (%) = $\{2[N_2]/[NO]^{in}\} \times 100$, NO conversion to N_2O (%) = $\{2[N_2O]/[NO]^{in}\} \times 100$, NO conversion to NO_2 (%) = $\{[NO_2]/[NO]^{in}\} \times 100$ and S_{N_2} (%) = $100 \times$ (NO conversion to N_2)/(NO conversion to $N_2 + N_2O$), where $[NO]^{in}$ is the reactor inlet NO concentration, and $[N_2]$, $[N_2O]$ or $[NO_2]$ is the concentration of N_2, N_2O or NO_2 in the reactor effluent gas.

3.2. The $C_3H_6 + O_2$ reaction

Fig. 4 depicts the effect of temperature on C_3H_6 conversion for the $C_3H_6 + O_2$ reaction at a constant reactor inlet composition of 1000 ppm C_3H_6 and 5% O_2 with the balance He. These conditions are similar to those applied for the investigation of the $C_3H_6 + NO + O_2$ reaction (1000 ppm C_3H_6/1000 ppm NO/5% O_2), but now NO is absent from the reactants. As shown in Fig. 4, the Pt-catalysed propene combustion is strongly temperature dependent, exhibiting sharply increased profiles upon increasing temperature. In particular, for the Na-free catalyst C1, propene conversion starts at a temperature of ~175 °C and reaches 100% at 240 °C. Similar to the case of $C_3H_6 + NO + O_2$ reaction, Na causes a significant promotional effect in catalytic activity of Pt for the propene combustion reaction, since the profiles of C_3H_6 conversion are significantly shifted to lower temperatures upon increasing Na content. Specifically, C3 catalyst offers 100% propene conversion at 175 °C, i.e. 65 °C lower to that of the Na-free catalyst. However, the effect of Na is

not again a monotonic function of its loading: catalyst C3 with 2.6 wt.% Na offers again the superior behaviour in C_3H_6 combustion, whereas Na loading beyond to this optimal value causes a significant suppression in C_3H_6 conversion performance (Fig. 4, C4 catalyst with 4.2 wt.% Na). That is, Na acts either as a promoter or as an inhibitor on the Pt-catalysed combustion of propene depending on its loading, in a very similar manner to the case of the $C_3H_6 + NO + O_2$ reaction described above.

A comparison of propene conversion profiles for all C1–C4 catalysts for the two reactions, i.e., $C_3H_6 + NO + O_2$ (Fig. 1a) and $C_3H_6 + O_2$ (Fig. 4), shows that in the latter case the propene conversion profiles stand at significantly lower temperatures than those of the analogous profiles of the former case: the presence of NO inhibits the Pt-catalysed propene combustion reaction. This inhibition is more obvious in Fig. 5 where the C_3H_6 *light-off* temperatures (i.e., the temperatures for 50% conversion of C_3H_6), T_{50}, for the two reactions are depicted for all catalysts C1–C4. Indeed, a significant shift of the curve that depicts the
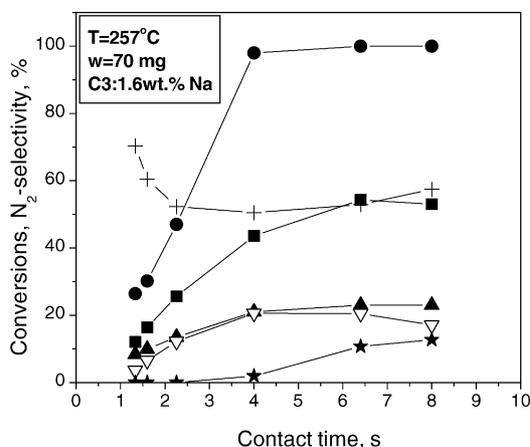
Fig. 3. $C_3H_6 + NO + O_2$ reaction. The effect of varying the reactant contact time τ, on the C_3H_6 conversion (●), total NO conversion (■), NO conversion to N_2 (▲), NO conversion to N_2O (▽), NO conversion to NO_2 (★) and N_2-selectivity (+) over catalyst C2 (1.6 wt.% Na) at 257 °C. Reactor inlet gas composition: 1000 ppm (v) NO, 1000 ppm (v) C_3H_6, 5% O_2; catalyst weight 70 mg. *Effective reactant contact time*, $\tau(s) = 2V_{H_2}(w/f)/([X]/10^6)$, where V_{H_2} (in cm^3/g_{cat}) is the H_2 uptake (Table 1), [X] (in ppm) the inlet gas phase portion of NO or propene, and w/f (in $[g_{cat}/(cm^3/s)]$) the reciprocal space velocity.

dependence of T_{50} with Na loading for the $C_3H_6 + O_2$ reaction to higher temperatures (ca. $\Delta T_{50} > 70\,^\circ C$) in the case of $C_3H_6 + NO + O_2$ reaction, is clearly obvious. This implies that NO acts as an inhibitor to propene combustion reaction at the whole range of experimentally accessible Na loadings. NO-induced inhibition of alkanes or alkenes oxidation over Pt has been reported in the literature [24,25,49,50].

3.3. The $NO + O_2$ reaction

Fig. 6 shows the effect of temperature on the NO conversion to NO_2, for the $NO + O_2$ reaction and the four C1–C4 catalysts listed in Table 1. For all catalysts NO_2

Fig. 5. The effect of Na loading of the catalyst on the C_3H_6 *light-off* temperature, T_{50}, for the reactions $C_3H_6 + NO + O_2$ and $C_3H_6 + O_2$. Conditions as in Figs. 1 and 4, respectively.

production begins at low temperatures (ca. 120 °C), then increases with increasing temperature up to a maximum value and finally decreases at elevated temperatures. The corresponding productions of N_2 and N_2O were found to be low, i.e., $N_2 + N_2O$ less than 5% in the examined range of temperature, and this is why they are not shown in Fig. 6. It is apparent that increasing Na content of the catalyst causes a systematic inhibition on Pt activity to produce NO_2 (Fig. 6).

It is interesting to compare Figs. 1a and 2c corresponding to $C_3H_6 + NO + O_2$ reaction and Fig. 4 corresponding to $C_3H_6 + O_2$ reaction, with Fig. 6 corresponding to $NO + O_2$ reaction. Comparison of Fig. 4 with Fig. 6 reveals that the two reactions ($C_3H_6 + O_2$ and $NO + O_2$) begin at similar temperatures (ca. 120 °C) over the Pt catalysts. Comparison of Fig. 2c with Fig. 6 shows that the presence of propene

Fig. 4. $C_3H_6 + O_2$ reaction. The effect of temperature on the conversion of C_3H_6 for the four catalysts of Table 1 with different Na loadings at constant reactor inlet gas composition of 1000 ppm (v) C_3H_6 and 5% O_2. Reactant *contact time* was kept constant at 4 s. Catalyst weight 70 mg.
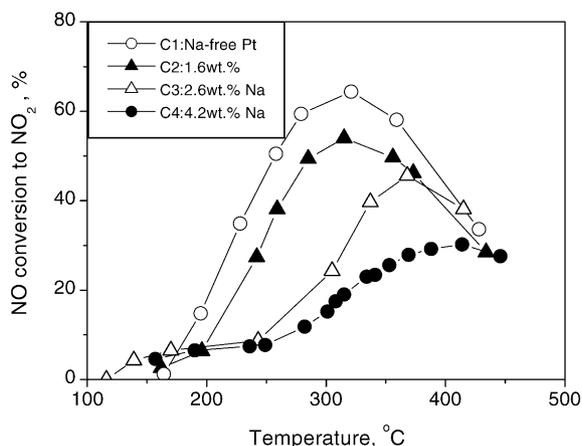
Fig. 6. $NO + O_2$ reaction. The effect of temperature on the conversion of NO to NO_2 for the four catalysts in Table 1 with different Na loadings at constant reactor inlet gas composition of 1000 ppm (v) NO and 5% O_2. NO *contact time* was kept constant at 4 s. Catalyst weight 70 mg.

completely suppresses NO_2 production (Fig. 2c) at low temperatures until the conversion of propene becomes 100% (Fig. 1a). In addition, note that this is in obvious contrast to the results obtained for the $NO + O_2$ reaction, where, in the absence of propene, remarkable amounts of NO_2 are produced at low temperatures (Fig. 6). This implies that propene acts as an inhibitor to $NO + O_2 \rightarrow NO_2$ reaction at low temperatures where its consumption is not complete.

4. Discussion

First we focus on the behaviour of the Na-free (unpromoted) Pt/γ-Al$_2$O$_3$ catalyst. The results of the present work show that this catalyst is very effective on the reduction of NO_x under conditions of excess oxygen in a considerably narrow temperature window. This is consistent with literature data [16–29]. Moreover, previous studies showed that Pt/Al$_2$O$_3$ has a negligible productivity of N_2 for the reduction of NO by propene in the absence of O_2. This *confirms* the relatively poor activity of this noble metal for the dissociative chemisorption of NO, which is well established in the literature [1,2,33–37]. However, Pt offered high N_2-selectivity for the reduction of NO by propene under conditions of excess O_2 [16–29], although, the window of considerably high conversion of NO to N_2 instead of other products (N_2O and NO_2) was found to be very narrow, standing at intermediate ($\sim$50%) propene conversions [16–29]. Our data that correspond to the Na-free Pt/γ-Al$_2$O$_3$ catalyst confirm all the above. In our previous kinetic studies on the C_3H_6 + NO reaction over polycrystalline Pt films [43] or dispersed Pt/γ-Al$_2$O$_3$ catalysts [33,36] we showed that the adsorption of C_3H_6 is much stronger than that of NO on Pt surface in a wide range of temperatures and partial pressures of reactant conditions. The present results not only corroborate this view but also indicate that propene adsorption is more pronounced compared to that of O_2. Indeed, the formation of NO_2 after the attainment of 100% conversion of C_3H_6 is in accord to this hypothesis.

Concentrating now on the behaviour of the Na-modified Pt/γ-Al$_2$O$_3$ catalysts, the following main experimental observations can be addressed:

(i) For low or moderate Na loadings the profiles of the C_3H_6 conversion are significantly shifted to lower temperatures upon increasing Na content of the catalysts. Consequently the temperature required for 100% C_3H_6 conversion is significantly decreased ($\sim$55 °C) due to Na addition (Fig. 1a). This implies a significant increase in the activity of Pt for the propene oxidation by NO and O_2 induced by Na addition.

(ii) Na-induced promotion on the conversion of C_3H_6 is always followed by a significant increase in the NO conversion at lower temperatures (Fig. 1b). Actually

C_3H_6 and NO conversions begin at the same temperatures.

(iii) The promotional effect of Na is not a monotonic function of its loading on the catalyst. A considerably narrow Na loading window around $\sim$2.6 wt.% optimizes the catalytic performance. Over-promotion (i.e., Na loadings beyond to this optimal value) causes severe inhibition in both C_3H_6 and NO conversions (Fig. 1a and b).

(iv) In comparison to the Na-free Pt/γ-Al$_2$O$_3$ catalyst, Na-promoted catalysts with loadings up to the optimal value exhibit significantly better productivity of N_2, together with an opening of the N_2-production window towards both lower and higher temperatures (Fig. 2a). At the same time the productivity of N_2O over Na-dosed catalysts is significantly suppressed and shifted to lower temperatures when Na loading increases (Fig. 2b). However, it is similar in shape to that of the Na-free catalyst. The beneficial effects of Na addition to the Pt catalyst regarding N-containing products distribution (i.e., better productivity of N_2 and suppressed productivity of N_2O), result on a significant improvement of N_2-selectivity (Fig. 2d).

(v) The production of NO_2 over the Na-modified catalysts appears when the conversion of C_3H_6 is completed, which is similar to what is observed in the case of the Na-free Pt catalyst. In addition, NO_2 production is significantly and monotonically suppressed as Na loading increases (Fig. 2c).

In our previous kinetics and spectroscopic studies of the NO reduction by C_3H_6 [33–38] we clearly showed that the addition of Na on Pt causes an increase in the strength of the metal–NO bond, accompanied by a weakening of N–O bond of the adsorbed NO molecules, thus facilitating NO dissociation. Both theory [51] and experiment [33–38,42–44,52] have shown that electropositive alkali promoters on Pt metal surfaces induce strengthening in the bonds of the metal–electron acceptor adsorbates (e.g., NO, O_2 and their dissociation products N and O) and weakening in the bonds of the metal–electron donor adsorbates (e.g., propene). This model can easily explain most of the above listed experimental observations. Thus, enhancement of the strength of the metal–NO bond causes an increase of the population (coverage) of the NO molecules on a catalyst's surface which is predominately covered with C_3H_6 and its derived species [22,33,36,43]. For a reaction of Langmuir–Hinshelwood type, i.e., with competitive adsorption of the reactants, the rate increases as the populations of the competitive species tend to be equal. In addition, the activity is *further* enhanced by the Na-induced NO dissociation [52] (this step is considered to be the key reaction-initiating step for the NO reduction process) as well as by the weakening of the metal–C_3H_6 bond [33–38]. All these factors operate together in increasing the reaction probability of NO and propene molecules (observations (i) and (ii)). Moreover, the observed

increase in N_2 production (observation (iv)) and decrease in N_2O production are consequences of the enhanced NO dissociation (due to Na addition), i.e., decreased concentration of molecular NO and increased concentration of atomic N on the surface. Both factors favor N_2 production rate at the expense of N_2O production rate, leading to higher N_2-selectivity (observation (iv)).

The question now is how Na addition affects O_2 adsorption which is also present in the reactive mixture and is expected to influence both C_3H_6 and NO coverages. Recent kinetic data for the $CO + O_2$ [44] and $C_3H_6 + O_2$ [53] reactions on Pt under electrochemical promotion by sodium were adequately explained by the proposal that the adsorption strength of the atomic oxygen on the catalyst's surface is enhanced by Na addition. Very recently this hypothesis has been confirmed by the TPD results of Vernoux et al. [48]. They found that the temperature of the oxygen desorption peak increases when Na loading of Pt catalyst increases. This observation offers direct evidence of the strengthening of the Pt–O bond. Because of the present experimental conditions of excess O_2, further increase of atomic oxygen species (in addition to those originated from NO dissociation) on Pt surface is expected which contributes to C_3H_6 conversion. Therefore, the effect of self-poisoning by propene and its decomposition products is counterbalanced. However, the present data cannot answer the question of which molecule's adsorption (NO or O_2) is favored by Na addition. Vernoux et al. [48] consider that O is a much stronger electron acceptor than NO, so O adsorption may be favored compared to NO adsorption.

Observation (iii) can be readily understood considering previous studies [43,53] where postreaction spectroscopic data indicate that the poisoning effect of Na at high loadings reflects the accumulation of alkali surface compounds which block the adsorption of the reactants on the surface. In particular, it was shown that in the presence of hydrocarbon species, at elevated temperatures, thick (three-dimensional) and stable films of Na_2CO_3 and $NaNO_3$ cover the surface thus inhibiting the reaction rates [43,53]. However, the observed inhibition at high Na loadings is probably the result of more than one effect. To be specific, O-poisoning of the surface, i.e., extended population of strongly bonded atomic O (in addition to strongly bonded NO and N) at the expense of propene due to the Na-enhanced adsorption of oxygen (and NO) may also contribute to the poisoning behaviour. This self-poisoning factor certainly acts in parallel with the active sites blocking by three-dimensional species, and is further discussed when a comparison of $C_3H_6 + NO + O_2$ and $C_3H_6 + O_2$ reactions is made.

Considering that in the presence of NO, O_2 and hydrocarbon, Na exists in the form of sodium nitrate/nitrite and carbonate species one wonders how it can act as a promoter. In our previous studies we assumed that CO_3^{2-} or NO_3^- counteranions exert a negligible opposite effect to

Na$^+$ cation mainly due to their larger size compared to the cation [37,38]. This hypothesis is in agreement to all our previous studies on alkalis and alkaline earths promotion of Pt-group metal de-NO$_x$ catalytic chemistry [31–38]. Formation of these compounds (Na_2CO_3 and $NaNO_3$) has significant negative effect only via sites blocking in the case of extended accumulation on the catalyst's surface (over-doped catalysts).

NO_2 appears when the conversion of C_3H_6 reaches 100%, i.e., when the probability of NO and O species to be found at adjacent surface sites increases. The monotonic decline of the NO_2 production upon increasing Na loading (observation (v), Fig. 2c) seems to reflect a self-poisoning effect of the $NO(a) + O(a) \rightarrow NO_2$ reaction induced by Na: mainly O-poisoning effect but the strengthening of the Pt–NO and Pt–N bonds may be considered as additional factors. Moreover, the expected higher rate of NO dissociation induced by Na (i.e., reduced population of molecular NO surface species) further contributes to the decline of the NO_2 production rate.

We now focus on the $C_3H_6 + O_2$ reaction. Previous studies of this reaction over Pt-film catalysts under electrochemically controlled promotion by sodium, via a Na$^+$ ion conducting solid electrolyte support (Na-β-alumina), showed that both promotional and poisoning effects induced by Na are possible when Na$^+$ is electrochemically supplied to the catalyst [53]. These effects depended on the amount of Na electrochemically supplied to the catalyst surface together with a notable dependence on reactant gas phase composition [53]. The present results (Figs. 4 and 5) show that at conditions of excess oxygen (5%) the Pt-catalysed propene combustion is also subjected to significant promotional and poisoning effects upon Na addition to conventional type catalyst (well dispersed Pt over γ-Al_2O_3). This Na-induced promotion on the Pt-catalysed propene combustion simply reflects the enhanced oxygen adsorption (due to Na) on the Pt surface predominantly covered by propene.

In the case of $NO + O_2$ reaction data show (Fig. 6) that NO_2 product appears even at low temperatures (ca. 120 °C) for all Na-free and Na-doped catalysts. It is emphasized here that test experiments involving the $NO + O_2$ reaction performed on Al_2O_3 and 2.6 wt.% Na/Al_2O_3 samples (i.e., without Pt) have shown much lower (in comparison to Pt-containing catalysts C1–C4) production of NO_2. Actually, the NO_2 productivity of these samples was less than 10% in the temperature interval of 100–500 °C. This implies that the NO + O reaction takes place mainly on Pt surface, which is in agreement to the mechanistic considerations for the hydrocarbon-SCR of NO$_x$ proposed by Burch and co-workers [20]. The data in Fig. 6 show that Na-free Pt/γ-Al_2O_3 catalyst is very effective for the oxidation of NO to NO_2 under conditions of excess O_2, while Na addition significantly suppressed NO_2 production due to the strengthening of the adsorption bonds of both electron-acceptor NO and O adsorbates.

A more detailed comparison of all three reactions investigated (C_3H_6 + NO + O_2, C_3H_6 + O_2 and NO + O_2) shows the following:

(i) Propene *light-off* temperature in the presence or in the absence of NO (Fig. 5): Although, in the promoting region of Na loading (0–2.6 wt.% Na), the degree of the Na-induced promotion on the C_3H_6 *light-off* temperature appears to be similar for both C_3H_6 + NO + O_2 and C_3H_6 + O_2 reactions (almost parallel *light-off* versus Na loading curves in the interval of 0–2.6 wt.% Na, with a difference of $\Delta T_{50} \approx 80$ °C, Fig. 5), this is not apparent in the poisoning region. In fact (Fig. 5, 4.2 wt.% Na) the induced degree of poisoning is significantly higher in the case of the former reaction thus resulting in a $\Delta T_{50} \approx 165$ °C. This difference on the degree of Na-induced poisoning in respect to the two different reactions may be rationalized as follows. According to the proposed model for the *mode* of action of the electropositive alkali promoter and the origin of poisoning phenomena, apart from the surface sites blocking by the formation of 3D species [43,53], a critical factor contributing to the poisoning phenomena is also the over-stretching (due to Na) of electron-acceptor adsorbates, i.e., NO and atomic N and O. Self-poisoning due to excessive adsorption of atomic oxygen at the expense of propene adsorption therefore takes place at this high Na loading for both reactions. However, in the case of C_3H_6 + NO + O_2 reaction it is reasonable to infer that part of the active Pt sites is occupied by more strongly adsorbed NO and atomic N. The latter species does not contribute to the propene combustion step. Consequently this acts in addition to the other two factors (i.e., site blocking by 3D surface complexes and O-poisoning) in decreasing the probability of the C_xH_y(a) + O(a) elementary step during the C_3H_6 + NO + O_2 reaction. In apparent contrast this additional factor does not exist in the case of C_3H_6 + O_2 reaction. Therefore, the net result of the simultaneous contribution of all these factors in the case of C_3H_6 + NO + O_2 reaction is a higher *degree* of poisoning compared to the C_3H_6 + O_2 reaction, as was indeed observed (Fig. 5).

(ii) NO-induced inhibition on the C_3H_6 *light-off* temperature (compare Figs. 1a and 4): this inhibition may be directly related to active sites occupation by adsorbed non-dissociated NO molecules together with atomic N produced by NO dissociation in case of Na-containing catalysts. The existence of these adsorbed species on Na-doped Pt surface during NO chemisorption has been confirmed experimentally by Harkness and Lambert [52]. The above species compete with the adsorption of atomic O on a Pt surface, predominantly covered by propene, thus decreasing the probability of the C_xH_y(a) + O(a) elementary step which leads to propene consumption. This is apparent by the shift of propene *light-off* to significantly higher temperatures for the case of C_3H_6 + NO + O_2 reaction (see Fig. 1a in comparison with Fig. 4, and Fig. 5). The formation of sodium nitrate/nitrite species [43,53] and the consequent surface sites blocking may also contribute to NO-induced inhibition on the propene oxidation, but this may be significant only in the case of extended accumulation on the catalyst's surface (i.e., for over-doped catalysts). Since NO_2 formation via NO(a) + O(a) is also possible during the propene-SCR of NO, this inhibition also indicates that the C_3H_6/O_2 reaction instead of the C_3H_6/NO_2 reaction is most likely to take place. The later view is in agreement with the explanation given by Chambers and Cant [49] for the observed NO-induced inhibition on alkanes oxidation over Pt/SiO$_2$. Similarly, Anderson et al. [50] in their study of a Pt/Ba/Al$_2$O$_3$ NO$_x$ storage catalyst concluded that desorption of NO_2 (previously stored in the catalyst) from the support undergoes reverse spillover onto the Pt surface which inhibits the activation of propene, thus explaining the observed shift of the propene *light-off* temperature to higher values. The hypothesis of the limited occurrence of the C_3H_6/NO_2 reaction is in accordance to the behaviour of NO_2 production in the presence or absence of propene. In the latter case (i.e., in the case of NO + O_2 reaction) data in Fig. 6 show that NO_2 production starts at low temperatures ($T \sim 120$ °C). On the contrary, when propene is present in the reaction mixture (i.e. in the case of C_3H_6 + NO + O_2 reaction, Fig. 2c), NO_2 product is not detected in the reactor outlet in this region where propene conversion is incomplete. In this case, strongly adsorbed propene, that decreases the probability of the NO and O adsorption at adjacent vacant sites, may be considered to inhibit the surface NO(a) + O(a) → NO_2 elementary step, since the hypothesis that the C_3H_6/NO_2 reaction is responsible for the absence of NO_2 in this region is inconsistent with previous explanations.

Finally, it is interesting to provide a closer comparison of the present results to those reported by Vernoux et al. [48]. They studied the same catalytic system under conditions that simulate diesel exhaust gas containing 2000 ppm C_3H_6/2000 ppm NO/5% O_2. Most of the Na-promotion characteristics obtained in the present work are, in general, in close agreement with those reported by Vernoux et al. [48]. However, in contrast to the data of Vernoux et al., we found that the promotional effects of Na are limited to a very narrow window of Na loadings (ca. 0–4.2 wt.% Na), attaining optimal promotion at 2.6 wt.%, whereas a loading of 4.2 wt.% Na is enough to cause almost complete inhibition on the de-NO$_x$ activity of Pt accompanied by a significant suppression of its activity to oxidize propene by O_2 or by NO + O_2 (Figs. 1 and 5). That is the promotional effects of Na can be altered to dramatic poisoning depending on its loading. This result is of great importance when applying the beneficial properties of Na promotion to the design of efficient catalyst formulations

for practical use. Na-induced poisoning phenomena were not observed by Vernoux et al. [48] even at loadings as high as 5 wt.% Na used in their study. The above difference can be readily understood in the following terms. According to the mode of action of Na-modifier proposed above, one could easily consider that an extension of the promoter-loading window to higher values might in principle be affected by the following factors: (i) the relative molar ratio of the electropositive (electron-donor) to electronegative (electron-acceptor) adsorbates imposed to the surface via the gas phase composition, i.e., in the present case the molar ratio of C_3H_6 to NO plus O_2, (ii) the *effective* promoter loading, i.e., the amount of the promoter that is in direct contact with the catalyst's surface instead of that which is accumulated on the Al_2O_3 support and is not expected to play any important role on the promotional phenomena, according to the proposed model. Simple calculations for the catalyst with the highest Na loading of 5 wt.% tested in the study of Vernoux et al. [48] (which showed the best promotion) taking into account its 0.9 wt.% Pt loading with a dispersion of 6%, the 5 wt.% Na loading, and the surface density of Pt crystallites ($d_{Pt} = 1.53 \times 10^{19}$ Pt-atoms/m^2 [33]), show that the *effective* Na loading is $\sim 1.9 \times 10^{-3}$ mmol *effective* Na/g_{cat}. This value is almost equal to that calculated for our catalyst C4 with 4.2 wt.% Na loading (i.e., 1.85×10^{-3} mmol *effective* Na/ g_{cat}) which exhibits the strong poisoning effects. However, the molar ratio of the electropositive to electronegative species, $C_3H_6/(NO + O_2)$, used in the work of Vernoux et al. [48] is equal to 2000/52,000 = 0.0385, that is almost double compared to that used in the present work (1000/51,000 = 0.0196). It is therefore reasonable to infer that the highest promoter loading of 5 wt.% Na used by Vernoux et al. still stands in the promoting region and larger amounts of promoter are necessary for their conditions in order to reach the poisoning region. The influence of the electropositive to electronegative molar ratio on the optimal promoter loading is further confirmed by the results of our previous work on Na-promoted Pt under simulated TWC conditions [38] where we found that Na loadings as high as 10.4 wt.% give the best promotion. In this work the molar ratio of electropositive to electronegative reactants was ~ 0.068, i.e., about four times higher than that of our present work and about twice than that used in the work of Vernoux et al. [48]. Further spectroscopic and kinetic studies are necessary in order to elucidate the role of the above factors on the promotional behaviour. Besides the greater understanding of electropositive promoters' mode of action in de-NO_x Pt-group metals catalytic chemistry, this could provide key design and operational controlling parameters for successful application of alkalis and alkaline earths promotion on the control of lean-burn and diesel engine exhaust gases.

5. Conclusions

Na addition substantially alters the performance of Pt/γ-Al_2O_3 catalysts under lean-burn conditions in terms of activity and selectivity in the SCR of NO by propene. Both promotion and inhibition may be observed, depending on Na loading.

Na promotes within a narrow window (0–4.2 wt.% Na), the optimum benefit being achieved at 2.6 wt.% Na (1.13×10^{-3} mmol *effective* Na/g_{cat}) under our conditions. Comparison with literature data indicates that optimal promotion is determined by promoter control of the relative coverages of electropositive (C_3H_6) to electronegative (NO and O) adsorbates.

NO inhibition of propene combustion may be understood in terms of NO_2 formation, which is less reactive towards the hydrocarbon, accompanied by a decrease in the available Pt sites for O adsorption due to competition from adsorbed NO and N.

Complete suppression of NO_2 at lower temperatures (incomplete propene conversion) is understandable in terms of the pronounced adsorption of the hydrocarbon under these conditions. This inhibits adsorption and dissociation of NO, and hence the formation of NO_2.

Generally speaking, the effects of Na may be rationalized in terms of alkali-induced inhibition or promotion of the chemisorption of electron-donating (C_3H_6) and electron-accepting (NO and O) adsorbates, respectively. Thus the same model for alkali promotion may be used to account for the behaviour under both lean-burn and stoichiometric exhaust conditions.

Acknowledgements

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