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The effect of potassium on the Ir/C_3H_6 + NO + O_2 catalytic system

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Abstract

The $C_3H_6 + NO + O_2$ reaction has been studied in a wide range of temperatures (ca. 250–400 °C) and oxygen concentrations (0–5% O_2) over potassium-modified Ir surfaces. The *in situ* electrochemical controlled concept of catalysts promotion was used by interfacing a polycrystalline Ir thin film with a potassium β''-Al_2O_3 solid electrolyte disc, a K^+ conductor. At low oxygen concentrations (i.e., at reducing conditions), the effect of potassium on the Ir activity and selectivity is negligible. However, at higher oxygen concentrations (oxidizing conditions), strong K-induced poisoning on both propene and NO turnover consumption rates, as high as ~85% and ~65%, respectively, were recorded. Significant reduction on the system selectivity towards N_2 was also recorded under these conditions (from 100% over K-free Ir surface to ~70% on K-modified Ir surfaces). The performance of Ir under alkali promotion is dramatically different to that reported in the literature for Pt or Pd under similar conditions, where strong promotional effects have been found. This very different behaviour may be understood in terms of the electronic influence of co-adsorbed potassium on the adsorption strengths of the neighbor reactants on the Ir surface.

Keywords: Iridium; Potassium; De-NOx; Selective catalytic reduction; Stoichiometric exhaust condition; Lean-burn conditions; N_2-selectivity

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1. Introduction

Pollution control of NOx, CO and hydrocarbons mainly produced by vehicles, but also by stationary sources, is the central environmental object. Although, three-way catalytic converters (TWCs) have been highly successful in controlling conventional engines' emissions that operate close to stoichiometric conditions, they are no longer efficient in controlling NOx emissions from lean-burn or diesel engines [1], which operate at net-oxidising conditions and are therefore related to excess oxidant concentrations in their exhaust gases (typically 350–1200 ppm NO, 2–12% O_2 [1]). The latter engines may be considered more promising compared to stoichiometric gasoline engines since they are related to significant lower fuel consumption. For NOx abatement in the presence of excess O_2, the selective catalytic reduction (SCR) of NOx by NH_3 over V_2O_5–WO_3–TiO_2 catalytic systems is a well-implemented technology for stationary sources. Overcoming the problems related to mobile sources, the NH_3-SCR technology is currently commercially available for trucks in the EU and for cars close to commercialization in the US. Another, convenient for mobile source, alternative technology for NOx abatement under excess oxygen that has recently gathered significant research efforts is the SCR of NOx with hydrocarbons [1,2]. A variety of catalyst formulations have been tested for this process, including primarily ion-exchanged zeolites based catalysts [2,3] and Pt-group metal supported catalysts [4–23].

Recent studies have shown that electropositive promotion, by alkalis or alkaline earths, induces significant enhancements in both activity and selectivity of Pt-group metals for the NO reduction by propene [10–18] or CO [17–20] in the absence [10–15] or in the presence of oxygen at lean-burn [16] or simulated stoichiometric TWC [17–20] conditions. Among the three noble metals Pt, Pd and Rh, studied up to now under electropositive promotion, the promotion was found to be more effective over Pt (up to two orders of magnitudes increases in NO reduction rate, accompanied by up to ~30–50 percentage points improvements in N_2-selectivity) [12–14,16,17], followed by Pd (up to one order of magnitude increases in NO

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reduction rate, accompanied by up to ~20–30 percentage points improvements in N_2-selectivity) [11,18], while on Rh, promotion was less effective and appeared only in the absence of oxygen (in the presence of oxygen, electropositive promoters were found to poison the NO reduction efficiency of Rh) [18]. Besides NO reduction by propene or CO, the oxidation of CO and hydrocarbons were also found to be significantly promoted over electropositive-modified Pt, Pd and Rh noble metals [16–18,21–23].

Iridium is an element of the noble metals family, which is currently under high research interest for the SCR of NOx [24–33]. Since now, there are only few preliminary studies concerning the influence of electropositive or electronegative promoters on its de-NOx chemistry: Vernoux et al. [32] have used the electrochemical promotion concept (or NEMCA effect, proposed by Vayenas et al. [34]) to show that the Ir-catalysed propene-SCR of NO under stoichiometric (2000 ppm C_3H_6, 2000 ppm NO, 1 vol.% O_2) and excess oxygen (2000 ppm C_3H_6, 2000 ppm NO, 5 vol.% O_2) conditions is subjected to moderate promotional effects with electronegative O^{2-} species, supplied to Ir catalyst via an YSZ solid electrolyte interfaced with it. Wögerbauer et al. [33] studied the lean NOx reduction at a specific simulated exhaust gas mixture (300 ppm NO, 1800 ppm C_3H_6, 450 ppm CO, 8 vol.% O_2, 10 vol.% H_2O, 10.7 vol.% CO_2) over electropositively modified by sodium Ir-black catalysts. However, since now, there are not any reports concerning the effect of electropositive promoters (alkalis) on Ir-catalysed NO reduction by hydrocarbons over a variety of oxygen concentrations and/or of promoter loading to the catalyst; note that the other noble metals (Pt, Pd and Rh) have shown very spectacular responses, strongly depended by these two factors.

In this study, we report on the influence of potassium on the Ir-catalysed NO reduction by propene in the presence of oxygen in a wide range of oxygen concentrations, including zero, around stoichiometric and excess O_2 conditions. The study was performed in a "single-pellet" type electrochemical reactor, where Ir catalyst in the form of thin film was interfaced with a potassium β''-Al_2O_3 solid electrolyte disk, a K^+ ions conductor. In this way, the electrochemical promotion (or NEMCA) concept was applied in order to investigate the performance of the $C_3H_6 + NO + O_2$ reaction on a variety of potassium coverages on Ir surface. The results obtained on the K-modified Ir catalyst were found to be in complete contrast to those previously found for Pt and Pd [10–18] under similar conditions, where the benefits of electropositive promotion were found to be very substantial; alkali-modified Ir performance seems to be more close to that of alkali-modified Rh [18]. The results may be understood in terms of the electronic effect of co-adsorbed potassium on the adsorption strength of the various reactants on the Ir surface. The explanations given are consistent to those that explain the very different behaviour on the other noble metals, Pt and Pd.

2. Experimental methods

The "single-pellet" reactor configuration (Fig. 1, top), used in most previous electrochemical promotion (EP) studies (e.g., [10,19,22]), was again applied in the present study: the potassium β''-Al_2O_3 disc was suspended in a 25 cm^3 quartz CST reactor with the three electrodes, i.e., working-catalyst electrode (Ir), counter (Au) and reference (Au) electrodes, all exposed to the reacting gas mixture (Fig. 1). The Ir catalyst film and the Au counter and reference electrode films were magnetron sputtered at the opposite sides of the beta alumina disc as schematically shown in Fig. 1 (bottom).

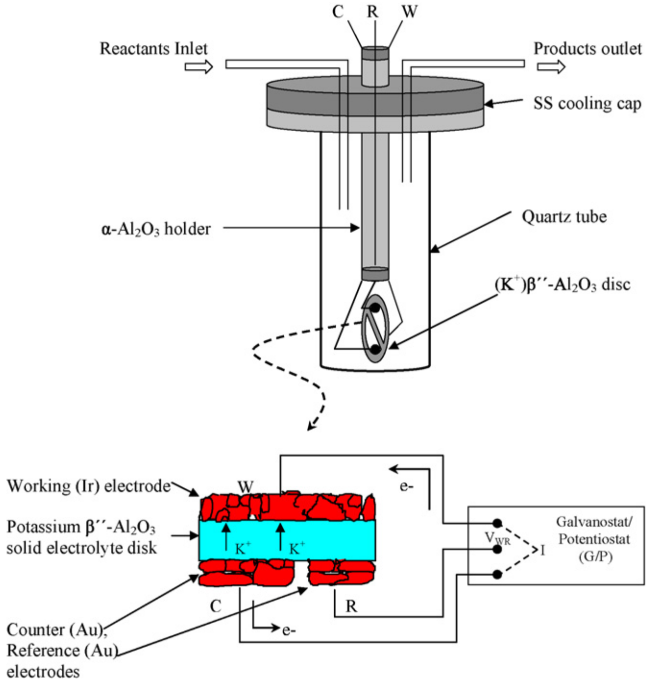

Fig. 1. Single pellet catalytic reactor and electrodes configuration.

Before measurements were taken, the catalysts were operated for 1 day in air and for 1 day in a reactive gas mixture, 2000 ppm NO/2000 ppm C_3H_6/5% O_2 at 420 °C in order to ensure stable operation (i.e., metal crystallite stabilization resulting from reaction or thermal sintering). The latter step is often used in Ir-catalysed de-NOx studies, since it has been documented that such a step activates the catalyst by establishing a certain ratio of Ir/IrO_2 (see for example Refs. [26,30,33]). After this pretreatment the true (active) surface area of Ir film was determined by m.s.-aided, CO temperature programming reaction (TPR) experiments, after CO adsorption at ambient temperature. This was found to be equal to 4.08×10^{-7} mol Ir or equivalently to 186 cm^2; the latter value was based on an Ir surface atom density 1.3×10^{19} $atoms/m^2$.

He-diluted Air Liquide certified gas mixtures (10% C_3H_6, 7.83% NO, 20.7% O_2 and 20% H_2) were used. After further dilution in ultrapure He (99.999%), in order to yield the required composition of 2000 ppm NO/2000 ppm C_3H_6/0–5% O_2, the gas mixture was delivered to the reactor by mass flow meters (MKS type 247) at 1 bar and a total flow rate of 140 cm^3/min.

The reactor inlet and outflow were on line analysed using a chemiluminescence NOx analyser (Thermo Environmental Instr., 42C, for the analysis of NO and $NOx = NO + NO_2$) and a

Shimatzu 14B gas chromatograph with TCD detector; the chromatographic separation of N_2, O_2 and CO was performed in a molecular sieve 5A column while CO_2, N_2O and C_3H_6 were separated in a Porapak-N column, both columns operated at 80 °C. N_2, N_2O, NO_2 and CO_2 were found to be the only N- and C-containing products; not NH_3 or CO were detected within the limits (<5–10 ppm) of our GC instrumentation. A mass spectrometer (Pfeiffer-Vacuum, Omnistar Prisma) was also used for simultaneous and continuous recording of AMUs 28 (N_2), 30 (NO), 32 (O_2), 42 (C_3H_6), 44 ($CO_2 + N_2O$) and 46 (NO_2).

Catalytic rate measurements under potentiostatic (steady-state) or galvanostatic (transient) conditions were carried out using a galvanostat–potentiostat (G/P, AMEL model 553). The galvanostatic transient behaviour of catalyst potential V_{WR} was used to calibrate the K coverage scale over a range of conditions, however, most experiments were carried out in the steady-state potentiostatic mode by following the effect of the applied potential between the catalyst and the reference electrodes (V_{WR}) on the reaction rate. The results are expressed in terms of turnover frequencies (TOF_i: molecules of the reactant i consumed or product i formed per surface Ir site per sec).

3. Results

3.1. Galvanostatic transient experiments

The electrochemical promotion (EP) concept of catalysts promotion provides a simple method for the direct correspondence of the promoter coverage on catalyst surface to the value of the catalyst potential V_{WR}, i.e., the potential difference between catalyst and reference electrode. The transient galvanostatic mode of operation of EP concept also provides a rapid method for assessing the response of the reaction rate to promoter coverage over a range of conditions (e.g., Refs. [19,21]). Such a galvanostatic transient at $T = 320$ °C and close to stoichiometric conditions, $S = 1.22$ ([NO] = 2000 ppm, $[C_3H_6]$ = 2000 ppm, $[O_2]$ = 1.0%) is depicted in Fig. 2. First the surface is electrochemically cleaned of potassium by applying a positive potential (V_{WR} = +600 mV) until the current ($I > 0$) between the catalyst and counter electrode vanishes. Then the galvanostat mode of the potentiostat/galvanostat (P/G) is used to impose a constant negative current $I = -200$ μA at $t = 0$. This corresponds to a flux of K to the catalyst surface at a rate equal $I/F = 2.08 \times 10^{-9}$ mol K/s. The corresponding K coverage on the Ir surface (θ_K) can therefore be computed from Faraday's law:

$$\frac{d\theta_K}{dt} = -\frac{I}{FN_0} \tag{1}$$

where N_0 (=4.08×10^{-7} mol Ir) is the number of available Ir sites independently measured by surface titration as described earlier. Thus the inserted precise θ_K abscissa in Fig. 2 can be constructed. Under these conditions, increasing θ_K on the Ir surface causes a decrease in the catalyst potential V_{WR} (and work function [34]) and a progressive suppression in propene oxidation and NO reduction turnover catalytic rates, $TOF_{C_3H_6}$ and TOF_{NO}, respectively (Fig. 2). At $\theta_K > \sim 0.9$, about 80% and 65% decreases in $TOF_{C_3H_6}$ and TOF_{NO}, respectively, have been reached; then the rates remain almost unaffected for higher potassium coverages. It is apparent that K acts as a strong poison for the hydrocarbon oxidation and de-NOx efficiency of Ir catalyst. Setting now $I = 0$ at $t = 5$ min, V_{WR} and rates remains unaffected (i.e., the amount of K transferred onto the surface remains constant affecting its performance). Setting finally the opposite current (I = +200 μA, at t = 10 min) the catalyst restores its initial un-promoted activity within few minutes (Fig. 2). The described transient behaviour is fully consistent with the steady-state behaviour of the catalyst (see below) that performed under identical conditions.

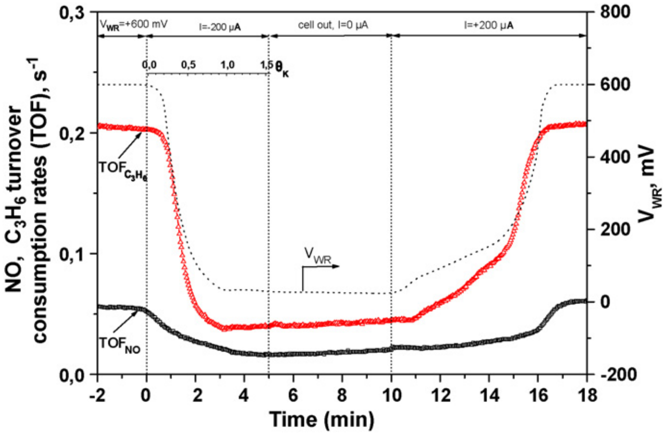

Fig. 2. Typical galvanostatic transient showing the C_3H_6 and NO turnover consumption rate and catalyst potential (V_{WR}) responses to step changes of applied current. $T = 320$ °C; [NO] = 2000 ppm, $[C_3H_6]$ = 2000 ppm, $[O_2]$ = 1.0% ($S = 1.22$, defined as $S = (2[O_2] + [NO])/9[C_3H_6]$); $F = 140$ cm^3/min.

3.2. Steady-state operation at constant imposed catalysts potentials

3.2.1. Effect of oxygen concentration

Fig. 3 depicts the influence of catalyst potential V_{WR}, or equivalently of potassium coverage θ_K, on the propene (Fig. 3a) and total NO (Fig. 3b) consumption turnover rates and on the corresponding selectivity towards N_2 (Fig. 3c) as a function of $[O_2]$ (the other reactant's concentrations were kept constant: [NO] = 2000 ppm, $[C_3H_6]$ = 2000 ppm) at $T = 320$ °C. The $TOF_{C_3H_6}$ curve at +600 mV (Fig. 3a), which corresponds to electrochemically clean (K-free) Ir, has a positive order dependence to oxygen at reducing conditions ($S < 1$) and then, for oxidizing conditions ($S > 1$) becomes zero order to oxygen concentration. The picture is strongly altered on K-modified Ir surfaces, where upon increasing $[O_2]$ and for $S > \sim 1$ the rates become negative order in oxygen, decreasing sharply until being stabilised at much lower levels; the higher the potassium coverage the lower the rate level. It is apparent from the data in Fig. 3a that alkali exerts in strong poisoning of the propene consumption rate, which is more pronounced at high O_2 concentrations (typically at $S > 1$). This poisoning is progressively increased upon increasing θ_K; for the maximum value of $\theta_K > 1$ used, an 88% reduction of the rate of propene

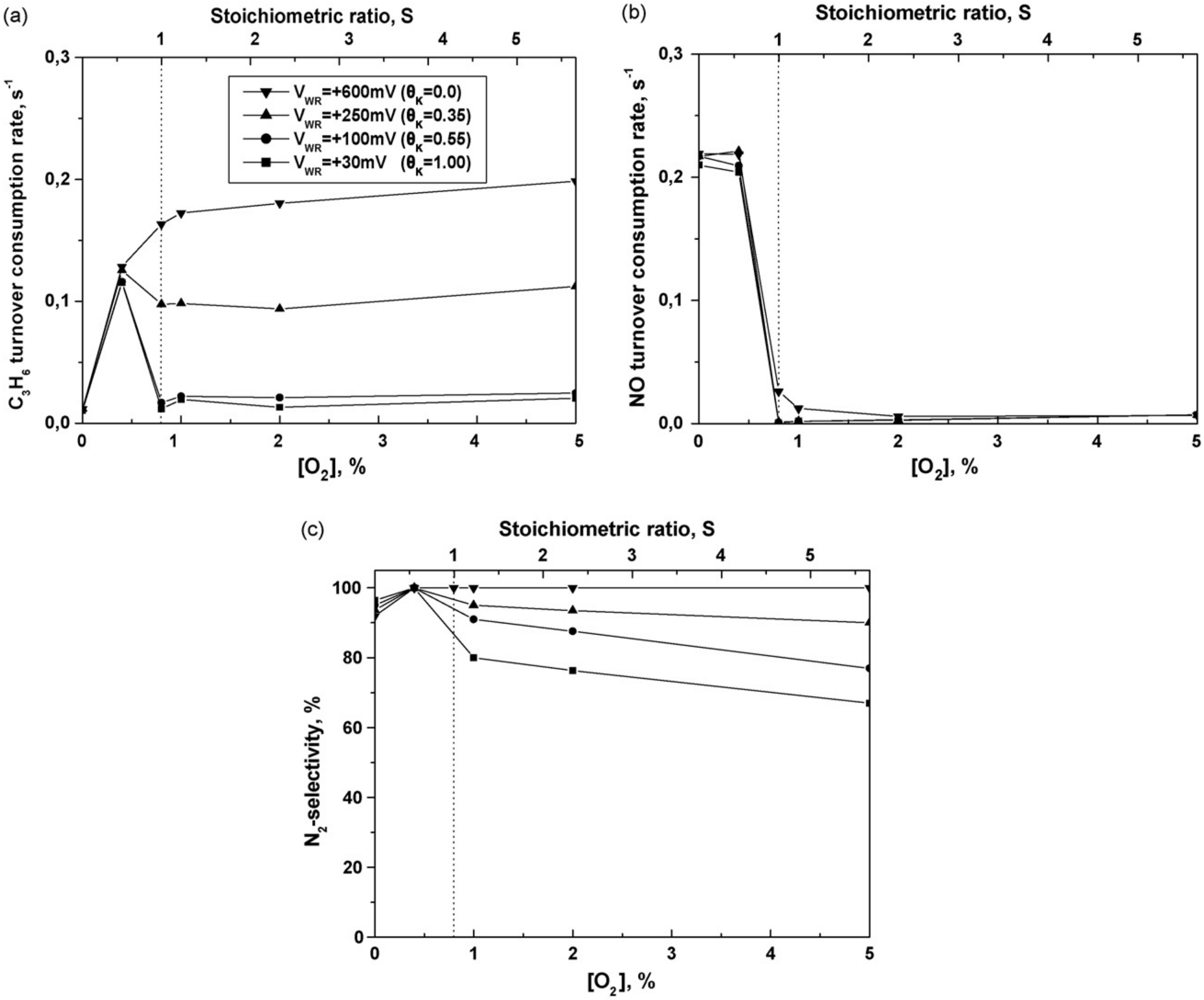

Fig. 3. The effect of oxygen concentration in the feed gas stream on the propene (a) and NO (b) turnover consumption rates and on the corresponding selectivity towards N_2 (c) at four different fixed catalyst potentials. $T = 320$ °C, [NO] = 2000 ppm, $[C_3H_6] = 2000$ ppm, $F = 140$ cm^3/min. The top abscissa depicts the stoichiometric ratio S.

consumption occurred. It is interesting, however, that for oxygen concentrations less than the stoichiometric point ($S < 1$) and in particular in the absence of oxygen ($[O_2] = 0\%$), the effect of potassium on $TOF_{C_3H_6}$ is negligible. On the other hand following the data of Fig. 3b (the dependence of NO turnover consumption rate on oxygen) a sharp decrease in the TOF_{NO} is observed for all cases (K-free and K-modified Ir) at the limit from net reducing to net oxidizing conditions ($S \sim 1$) due to the competition with the excess oxygen present. Comparing the TOF_{NO} curve that corresponds to clean Ir to the curves that correspond to K-modified Ir, a poisoning influence induced by potassium is again obvious in the overall S interval investigated (Fig. 3b). Concentrating now on the system selectivity towards to N_2 (Fig. 3c), we can observe that besides the case of zero oxygen content in the feed (i.e., the C_3H_6 + NO reaction), where the selectivity of K-free Ir is ~90%, the presence of oxygen in the gas mixture makes Ir very selective to N_2 formation. Its selectivity was stabilised at 100% for all the rest range of $[O_2]$. Interestingly, besides the point of zero oxygen concentration, where a K-induced enhancement in N_2-selectivity is observed, in the presence of oxygen, K-modified Ir surfaces apparently have significantly lower values of N_2-selectivity (Fig. 3c). This indicates that the high efficiency of clean (K-free) Ir surface to adsorb NO in a dissociatively manner, is reduced on K-modified Ir surfaces when oxygen is present.

3.2.2. *Effect of temperature*

Fig. 4 depicts the influence of catalyst potential V_{WR} on the CO_2 (Fig. 4a) and N_2 (Fig. 4b) turnover formation rates and on the corresponding N_2-selectivity (Fig. 4c) at constant feed composition ([NO] = 2000 ppm, $[C_3H_6] = 2000$ ppm, $[O_2] = 1.0\%$; $S = 1.22$) for four different catalyst temperatures—in every case the rate decreases significantly with decreasing catalyst potential. The top abscissa shows the approximate linearized potassium coverage scale (θ_K^*) derived from a separate galvanostatic transient, by determining the length of time required for a constant current ($I = -200$ μA) to change

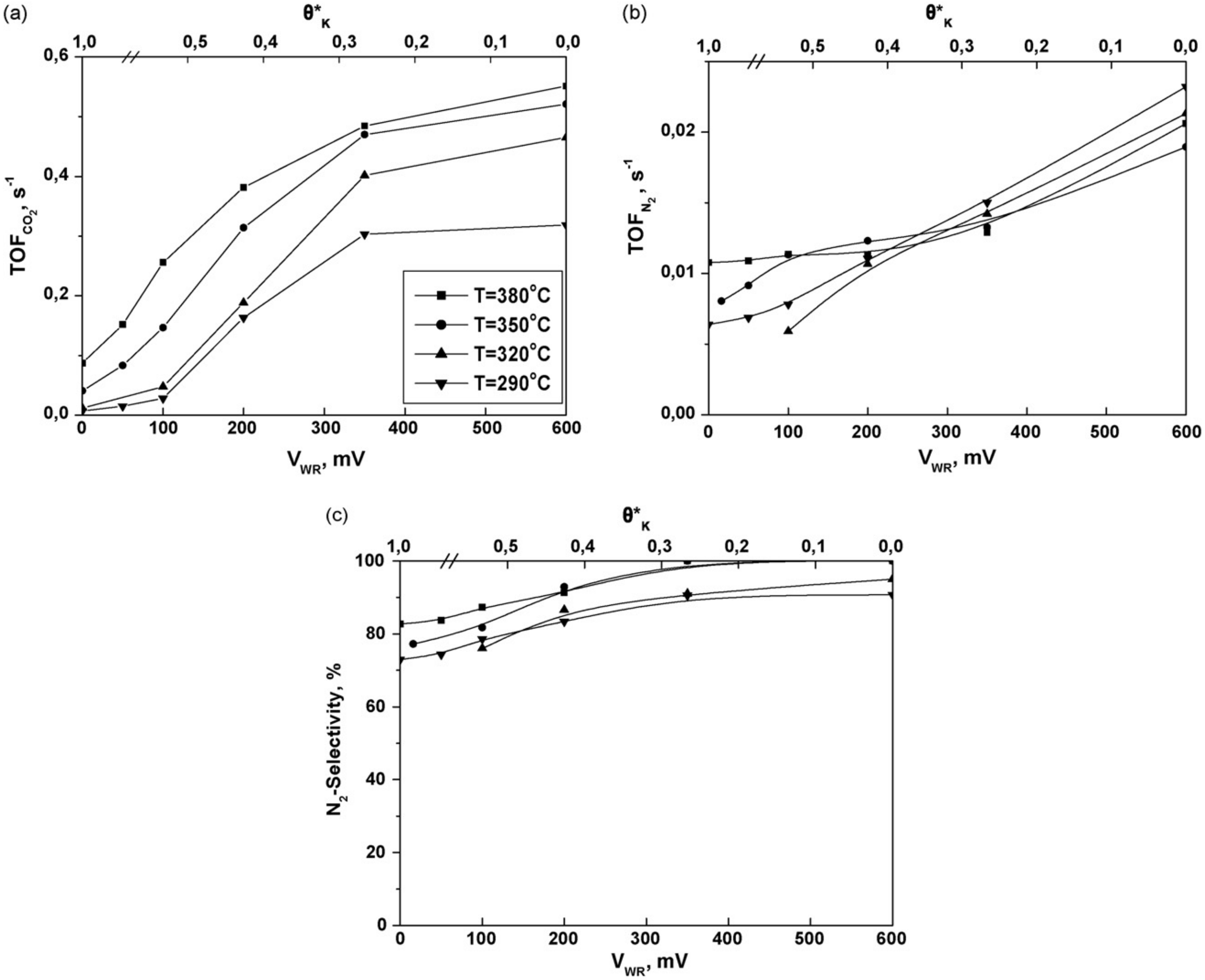

Fig. 4. The effect of catalyst potential V_{WR} on the CO_2 (a) and N_2 (b) turnover formation rates and on the corresponding selectivity towards N_2 (c) at four fixed catalyst temperatures. [NO] = 2000 ppm, [C_3H_6] = 2000 ppm, [O_2] = 1% (S = 1.22), F = 140 cm^3/min. The top abscissa depicts the approximate linearized potassium coverage θ^*_K (see text for discussion).

V_{WR} from the clean surface value of +600 mV to the value of interest. The data of Fig. 4 clearly shows the poisoning effect of K on the Ir/C_3H_6 + NO + O_2 catalytic activity at all temperatures investigated.

Fig. 5 shows Arrhenius plots of the CO_2 (Fig. 5a) and N_2 (Fig. 5b) turnover formation rates at four different values of catalyst potential V_{WR} (or θ_K) over the temperature interval 250–450 °C. The corresponding behaviour of N_2-selectivity versus 1/T is shown in Fig. 5c. Data were acquired at a fixed feed composition simulating lean-burn conditions ([NO] = 2000 ppm, [C_3H_6] = 2000 ppm, [O_2] = 5%). Even at this excess oxygen composition the performance of the system upon K addition is in general similar to that obtained for stoichiometric oxygen conditions (e.g., Fig. 4); The strong poisoning effect of potassium addition on the CO_2 turnover formation rate (i.e., propene consumption rate) as well as on the N_2 turnover formation rate (or NO consumption rate) over the whole temperature interval investigated, is obvious (Fig. 5a and b, respectively). The corresponding selectivity is also decreased monotonically with increasing θ_K (Fig. 5c), although at very high temperatures all cases approach the selectivity value of 100%.

4. Discussion

As discussed in our previous studies [10–14,16,17,19–22], electropositive promoters (alkalis and alkaline earths) on Pt-group metal surfaces induce strengthening in the chemisorptive bonds of electron acceptor adsorbates (such as CO, NO, O_2 and their dissociation products), promoting their adsorption, and weakening in the chemisorptive bonds of electron donor adsorbates (e.g., alkenes). These effects are due to the action of the electrostatic field of the electropositive modifier on adjacent co-adsorbed molecules and have received a detailed theoretical analysis by Lang et al. [35]. In addition to the theoretical calculations of Lang et al., clear experimental evidences for these effects have also been reported: *in situ* DRIFTS studies by Koukiou et al. [36] concerning the interaction of NO with alkali-dosed Pt(Na)/Al_2O_3 catalysts have shown pronounced and progressive red shifts of the N–O stretching frequency

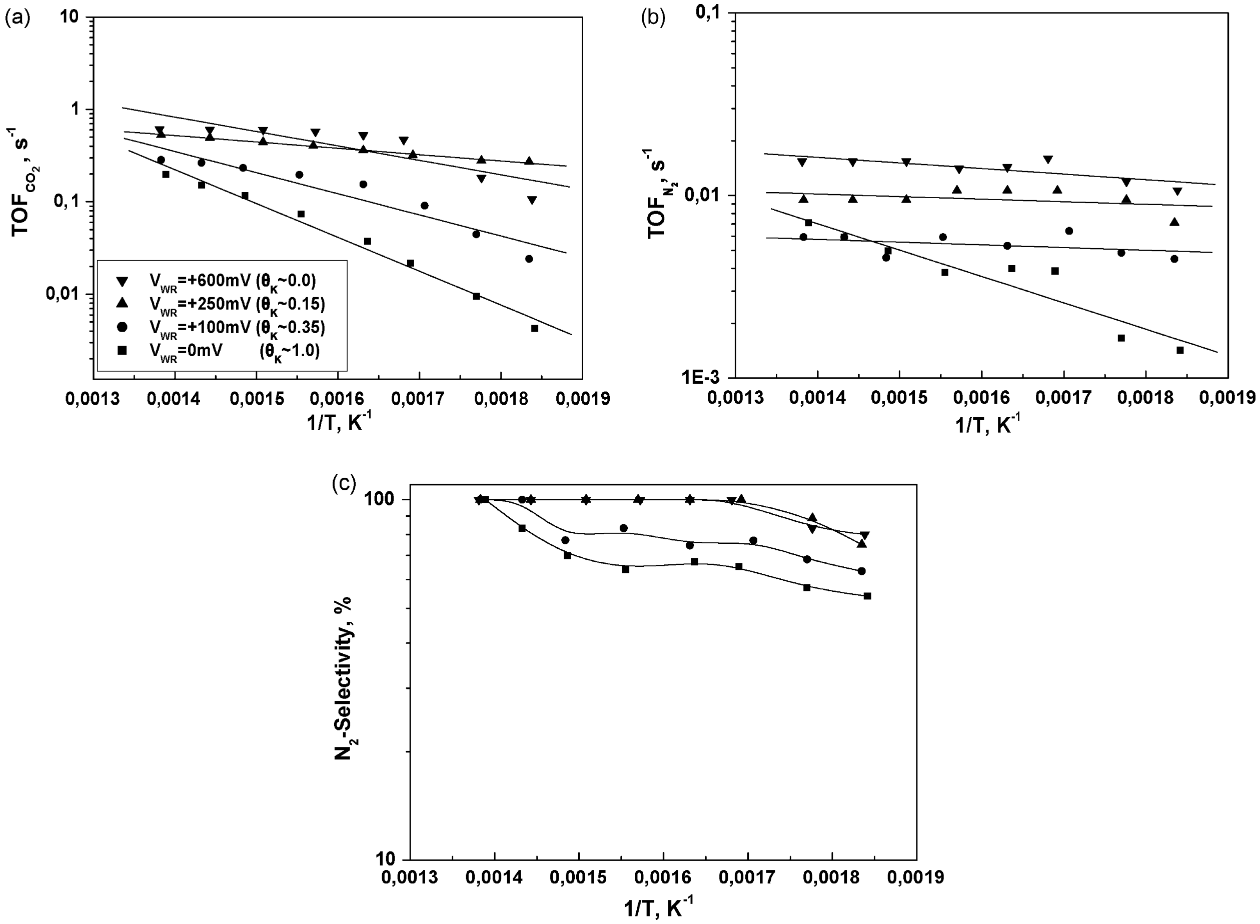

Fig. 5. The effect of temperature (Arrhenius plots) on the CO_2 (a) and N_2 (b) turnover formation rates and on the corresponding N_2-selectivity (c) at several fixed catalyst potentials and potassium coverages on Ir surface. Conditions: [NO] = 2000 ppm, [C_3H_6] = 2000 ppm, [O_2] = 5% (*S* = 5.67); *F* = 140 cm^3/min.

associated to molecular NO adsorbed on the Pt component of the Na-modified supported catalyst; TPD studies of the NO adsorption on Na-dosed Pt{1 1 1} single crystal by Harkness and Lambert [37] have shown enhanced NO adsorption and extended alkali-induced NO dissociation; Vernoux et al. [38] reported Na-induced strengthening of the Pt–O as confirmed by O_2-TPD studies on Na-modified Pt/Al_2O_3; red shifts of the CO stretching frequency associated with CO adsorbed on K-modified Pd catalysts have also been reported by Liotta et al. [39].

Accordingly to the above-described effects in the case of NO, for example, the electrostatic field of adjacent electropositive modifier lowers the energy of the NO π^* antibonding orbital in respect to the Fermi level. This apparently involves a lowering of the noble metal work function by the electropositive modifier. It also causes increasing charge transfer from the metal to the NO π^* orbital, resulting in enhanced metal–NO bond strength and decreased N–O bond strength of the adsorbed NO molecule: this enhances NO adsorption and apparently promotes its dissociation.

Based on the above effects of electropositive promoters to the chemisorptive properties of oxidant and reductant adsorbates on noble metal surfaces, the substantial promotional effects induced by alkalis on the hydrocarbon-SCR of NO over Pt, Pd or Rh have been consistently interpreted [10–23]. Therefore, for Pt or Pd catalysts, where the propene adsorption is very strong [10–12] inhibiting the adsorption of oxidants (NO or O), the addition of electropositive promoters results in a weakening of the metal–propene bond and a strengthening on the metal–oxidant bond. This reduction in poisoning, due to the strong adsorption of the hydrocarbon, acts synergistically with the enhancement on the adsorption of the oxidants – previously limited because of the former – allowing all the participating reactions (the hydrocarbon and CO oxidation and NO reduction) to proceed more efficiently. This rate enhancement is getting higher with increasing the promoter loading, reaching a maximum value, and then declines in the region of over-promotion: the advantages gained due to the increased NO adsorption/dissociation and weakened H/C sorption strength are now reversed due to the stronger sorption of NO dissociation products (N and O) and the resulted O-poisoning. This explains the experimentally observed maxima during electropositive promotion of Pt and Pd as a function of the promoter loading [10–14]. On the other hand, in the case of Rh, the adsorption of electronegative species (NO, O_2 and CO) is significantly stronger than on Pd or Pt [40], favoring the balance of electropositive (e.g., propene) and electronegative (NO, O) adsorbates coverages towards to the latter. Thereby, poisoning effects, due to predominant adsorption of propene, that occurs in the case of Pt and Pd, do not at work on Rh catalyst. According to this scenario Macleod et al. [18] have explained the adverse behaviour of Rh catalyst in comparison to that of Pd (or Pt) under Na-promotion for the propene-SCR of NO under simulated TWC conditions. They argue that the observed strong poisoning of the propene oxidation over Rh induced by Na addition to the catalyst simply reflects further shift of the surface species balance to the wrong direction, i.e., towards to oxidants at the expense of propene adsorption (i.e., NO and O poisoning of the surface). We agree with this explanation. Recalling the similarities of the de-NOx process characteristics of Rh and Ir, in contrast to that of Pt and Pd, it is reasonable to suggest that similar phenomena are at work here and the influences of the alkali on Ir de-NOx catalytic chemistry can receive similar explanations.

Therefore, the de-NOx catalytic chemistry characteristics of potassium-modifier Ir surfaces may be rationalized according to the following terms. The addition of potassium on Ir surface enhances the adsorption of NO and O at the expense of propene. Therefore, at oxidizing atmospheres ($S > 1$) the addition of K strongly poisons the hydrocarbon oxidation due to the stronger adsorption of oxidant adsorbates, which is additionally aided by their favored distribution in the gas phase. This results to an extended shift of the surface species balance towards to oxidants at the expense of propene adsorption (i.e., O-poisoning of the surface), as indeed manifested by the negative order dependence of the propene consumption rate with increasing $[O_2]$ over K-dosed Ir (Fig. 3a). As O coverage is built up due to increasing K-coverage, Ir metal is eventually oxidized to IrO_2; the stronger the Ir–O bond strength the higher IrO_2/Ir ratio on the catalyst surface. Both these entities are in equilibrium at the reaction conditions under consideration and their ratio is strongly depended on O coverage and crystallite size (e.g., Refs. [29,31,33]). Since IrO_2 is essentially inactive to hydrocarbon-SCR of NOx [24–31,33] this explains why the turnover rates of propene and NO consumption are stabilised at progressively lower value levels upon increasing K-coverage of the surface (Fig. 3a and b).

The surprising, at first sight, decrease in N_2-selectivity as a function of potassium coverage (Figs. 3c, 4c and 5c), which is, in principle, contradictory to that observed on alkali-modified Pt and Pd surfaces under similar conditions [10–20] and to theoretical [35] and experimental [36,37] evidences that alkali promote NO dissociation, certainly deserves explanation. The substantially enhanced N_2-selectivity over alkali-modified Pt and Pd was rationalized in terms of the following reaction scheme [10–20].

Alkali addition enhances the dissociative chemisorption of NO according to the step:

$$NO_{ads} \rightarrow N_{ads} + O_{ads} \qquad (2)$$

While O_{ads} is scavenged by adsorbed hydrocarbonaceous species to produce CO_2 and H_2O, nitrogen and nitrous oxide are produced by N_{ads} recombination or by $N_{ads} + NO_{ads}$ reaction, respectively:

$$N_{ads} + N_{ads} \rightarrow N_2(g) \qquad (3)$$

$$N_{ads} + NO_{ads} \rightarrow N_2O(g) \qquad (4)$$

In the case of Pt and Pd, enhancements in N_2-selectivity were therefore understandable as a consequence of the alkali-promoted dissociative chemisorption of NO in the presence of strongly adsorbing propene: decrease and increase, respectively, in the amounts of molecularly adsorbed NO and atomic N_{ads} on the surface (step (2)), thus favoring step (3) over step (4). Someone might now wonder what is the key-difference in the case of Ir responsible for the contradictory behaviour to Pt and Pd in respect to N_2-selectivity under similar conditions. Recall here the following significant experimental observations of the present results: In the absence of oxygen and net reducing conditions, i.e., for the $C_3H_6 + NO$ reaction (at $[O_2] = 0$ in Fig. 3b), the NO reduction rate is much higher than that in the case of net oxidizing conditions, and, the addition of potassium to Ir did indeed cause small but significant improvements in N_2-selectivity (Fig. 3c, at $[O_2] = 0$). Potassium addition is detrimental to N_2-selectivity when oxygen is present (Figs. 3c, 4c and 5c). All these experimental observations imply that the presence of oxygen plays a key-role for the observed performance of selectivity over K-modified Ir. It is well known from the literature that high oxygen coverages on a noble metal surface strongly inhibit NO dissociation [31,41]. It is also manifested, that poisoning of the Ir catalyst for NO reduction and its selectivity towards N_2 starts from low O coverage on the Ir surface [31]. Accordingly, the addition of potassium to Ir seems to have two contradictory effects in respect to N_2-selectivity: (i) improvement of the NO dissociation (which is, in principle, substantially high over alkali-free Ir) at negligible coverages of O on Ir surface, and (ii) inhibition of NO dissociation due to O-poisoning occurs at elevated O coverages on the surface. Thus the value of the selectivity is strongly depended on the balance of these two factors. On K-dosed Ir surfaces, at zero oxygen in the feed gas factor (i) is favored and the selectivity is increased, whereas in the presence of gaseous oxygen factor (ii) is favored and the selectivity is reduced, according to the present experimental observations.

Most of the characteristics of the influence of potassium on the Ir-catalysed NOx reduction by propene observed here are in very close agreement to that observed by Baiker and co-workers [33] studying the influence of sodium on the SCR of NOx over Ir black catalyst under a simulated exhaust gas mixture containing 300 ppm NO, 1800 ppm C_3H_6, 450 ppm CO, 8 vol.% O_2, 10 vol.% H_2O, 10.7 vol.% CO_2: similarly to the present results, they indeed observed significant inhibition of the propene oxidation and NO reduction efficiency of Ir induced by Na addition. The only noteworthy difference concerns the selectivity towards N_2. Contrary to the present results, the authors have found improvements in selectivity (at $T > 300\ ^{\circ}C$) due to Na addition. This contradiction is most probably because of the following points. Their selectivity calculations are based on an expression that involves NO_2, which was found to be a significant by-product, ignoring N_2O, which was found to be produced only in trace amounts—hardly reaching the limit of quantification. In our case, only trace amounts of NO_2 were detected and only at very high temperatures (this is why it was ignored from the selectivity calculations) while N_2O was clearly detectable. These differences in the distribution of N-containing products between the two studies are most likely due to the very different gas mixture feed used. The existence of CO in the feed composition used in Ref. [33] – the adsorption of which is strongly enhanced by alkali addition [19–21,39] – is probably the key point, although, influences due to the existence of excess H_2O and CO_2 could also be considered. Due to the system complexity, the influence of these molecules is difficult estimated. However, since these entities are present in remarkable amounts in exhaust streams, future extension of the present study in this direction may be interesting.

5. Conclusions

Addition of potassium to Ir catalyst during the $C_3H_6 + NO + O_2$ is detrimental for both propene oxidation and NO reduction efficiency and N_2-selectivity of the catalyst for all oxygen concentrations up to very excess oxygen; the only case were the catalytic system is practically unaffected by potassium poisoning is at zero oxygen concentrations, i.e., at net reducing conditions where a slight promoting effect on the N_2-selectivity but not on the rates was observed. These effects are due to excessive enhancement of oxygen adsorption on Ir surface in the expense of the hydrocarbon adsorption (O-poisoning of the surface). The same factor, i.e., strongly adsorbed oxygen on the surface, is responsible for the worse selectivities observed over K-dosed Ir surfaces in comparison to K-free Ir.

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