Effect of sodium on the catalytic properties of iridium black in the selective reduction of NO_x by propene under lean-burn conditions

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The effect of sodium promotion on the performance of an iridium black catalyst for the selective catalytic reduction of NO by propene has been investigated. Sodium loadings above 1 at% were found to increase the nitrogen selectivity close to 100% in the whole temperature range investigated (150–450 °C). However, the presence of Na shifted the on-set of all reactions to higher temperatures (*ca.* 20–50 °C for the highest promoter loadings, *i.e.*, 10 at% Na), leading to a narrowing of the operation temperature window. Consequently, moderate sodium loadings in the range of 1–3 at% represent the best compromise for a beneficial application of iridium in $DeNO_x$ catalysis. Combined thermogravimetry–mass spectrometry investigations revealed that not only NO dissociation, but also, *e.g.*, the decomposition of propene and the adsorption of oxygen as well as the oxidation of iridium are influenced by the presence of sodium. Mechanistically, our observations are consistent with a model, where the removal of adsorbed oxygen could represent the rate-limiting step under the applied conditions.

KEY WORDS: lean $DeNO_x$; HC-SCR; NO reduction by propene; promoter effects; sodium carbonate; iridium catalysts; pulse thermal analysis; propene decomposition; nitrogen selectivity

1. Introduction

The selective catalytic reduction of nitric oxide by hydrocarbons (HC-SCR) represents a future alternative for the purification of exhaust gases under lean-burn conditions (see, *e.g.* [1–4] and references therein). Recently, iridium turned out to be a highly active and selective metal for this reaction. Its performance, however, depends strongly on the particle size and on the conditioning procedure [5–9]. As part of a comprehensive study on $DeNO_x$ catalysis (see, *e.g.* [10–12] and references therein), we recently reported on the preparation and activation of suitable Ir/H-ZSM-5 [7] and Ir black catalysts [9]. During our experiments we investigated some samples which were later found to contain contamination of sodium compounds. Several studies on effects arising from alkali adatoms on the catalytic NO reduction have been published previously for other platinum metals (see, *e.g.* [13] and references therein). The results of the latter investigations, however, differed significantly, depending on the employed metals and specific reaction conditions. On the one hand, Lambert and co-workers, *e.g.*, reported a significant enhancement for the NO, CO, and propene conversion (evaluated *via* the temperature at the on-set of each reaction and at 50% conversion, respectively), as well as for the nitrogen selectivity by sodium over supported Pd [14] and Pt catalysts [13] (reactant concentrations for the latter study were 0.1% NO, 0.11% propene, 0.7% CO, and 0.78% O_2). On the other hand, Burch and Watling found detrimental effects on the maximum degree of NO conversion over Pt/Al_2O_3 in the presence of Cs and K, and observed virtually no effect on the selectivity (0.1% NO, 0.1% propene, and 5% O_2 [15]). Likewise, Shinjoh *et al.* noticed a negative effect of alkali metals on the propene conversion at 300 °C over a Pd/Al_2O_3 catalyst (0.12% NO, 570 ppm propene, 0.33% H_2, 1% CO, 0.46% O_2, 10% CO_2, and 3% H_2O [16]). This discrepancy stimulated a detailed investigation of sodium promotion for iridium catalysts, since the ensuing effect could not be simply deduced from the results with the other metals.

Here we will first compare the dependence of the activities of all participating reactions, as well as of the nitrogen selectivity, on the sodium content of iridium black. It will be demonstrated that the selectivity strongly benefits from the presence of the Na promoter, while the activity is only slightly, but adversely affected. Subsequent pulse TG measurements reveal that the presence of sodium not only influences NO dissociation, but also affects the decomposition of propene and the adsorption of oxygen and iridium oxidation, respectively. Finally, we will discuss mechanistic implications for the NO reduction over iridium under the applied reaction conditions in the light of recent studies on Na promotion of platinum group metals.

2. Experimental

The promoted Ir samples were prepared by suspending ∼250 mg Ir black powder (Alfa Aesar) in *ca.* 3 ml of an aqueous solution, containing the appropriate amount of sodium carbonate. Under stirring, the water was evaporated

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Table 1
Effect of sodium on the activity (evaluated *via* the temperature necessary for 20[a], and 50% NO conversion – relative to the maximum conversion level of each sample), and crystallite sizes measured before and after reaction by XRD.

Na (at%)	T_{onset} (°C)	$T_{50\%}$ (°C)	d_{Ir} (nm) by XRD Before reaction	d_{Ir} (nm) by XRD After reaction
0	255	310	13	15
0.1	280	320	13	14
0.3	290	335	14	17
1	321	340	14	17
3	330	355	16	18
10	330	350	16	16

[a] The temperature for 20% NO conversion is termed T_{onset}.

by heating at ambient pressure, and the catalysts were finally dried at 120 °C in air. Using supported catalysts for promotion has the disadvantage that always an unknown but possibly substantial part of the promoter will be situated on the support. With Ir black we avoid this problem and can investigate the influence of the promoter species on the catalytic performance on the metal alone. The actual sodium loadings were derived gravimetrically because spectroscopic methods could not be applied due to the incomplete dissolution of iridium black by standard digestion methods. Prior to reaction, the samples were reduced at 300 °C in 6% H_2 for 30 min (balance nitrogen, 450 Nml/min). The reaction was carried out in a quartz tube reactor, starting at 150 °C, by increasing the temperature stepwise by 50 °C after 60 min at each setpoint. As can be seen from table 1, the presence of the promoter species exhibited no significant influence on the structural properties of the catalyst during pretreatment and reaction (except a small increase of the crystallite size from 13 to 16 nm). Each reactor loading contained 7.5 mg of iridium powder, fixed by quartz wool plugs. The catalysts were diluted with silica powder (*ca.* 1 : 20) in order to guarantee plug-flow conditions. The simulated exhaust gas mixture consisted of 300 vpm NO, 0.18 vol% propene, 450 vpm CO, 8 vol% O_2, 10 vol% H_2O, 10.7 vol% CO_2, and balance N_2 (450 Nml/min). Reactant/product concentrations were followed by on-line FTIR analysis. A more detailed description of the setup is provided in [10]. All nitrogen-containing compounds except N_2 are detectable with this setup down to concentrations of a few ppm. The only nitrogen-containing compounds which have been detected during the experiments were NO, NO_2, and traces of N_2O. The outlet concentrations of these compounds together with the feed concentration of NO were used to perform a nitrogen balance. XRD spectra were recorded on a Siemens D5000 powder X-ray diffractometer in a step mode (step size 0.01°, 2 s/step) using Ni-filtered Cu K_α radiation (35 mA, 45 kV). The mean Ir crystallite size was calculated from the Ir(111) reflection, using the Scherrer equation. Pulse thermal analysis (PulseTA) experiments were carried out on a Netzsch STA 409 thermoanalyzer, connected to a mass spectrometer (Baltzer QMG 420) by a heated stainless steel capillary. Previous to the impregnation with sodium carbonate, the catalysts, used in the TGA experiments, were sintered in helium at 750 °C, yielding a mean crystallite size of 28 nm for all samples. Further details on the thermogravimetric (TG) setup can be found in [17]. Note that sodium carbonate decomposes thermally only at temperatures above 800 °C (unpublished results) and thus is not expected to cause background contributions for the observed CO_2 evolution in TG-MS pulse experiments.

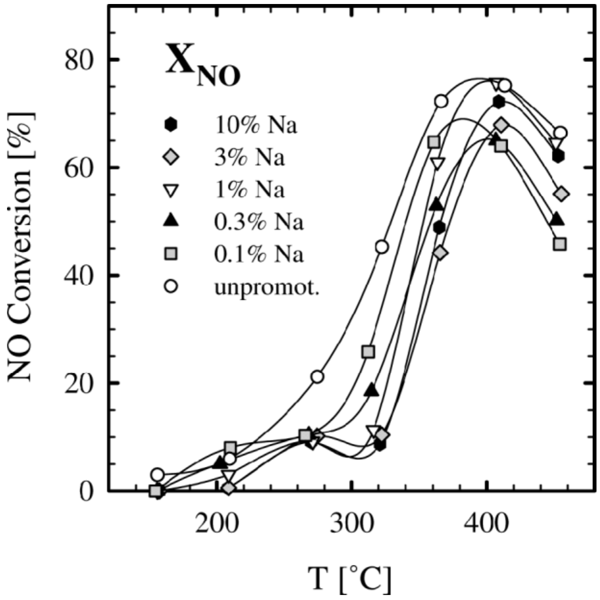

Figure 1. NO conversion over Ir black catalysts with different loadings of the sodium promoter as a function of temperature in a simulated exhaust gas mixture of 300 vpm NO, 0.18 vol% propene, 450 vpm CO, 8 vol% O_2, 10 vol% H_2O, 10.7 vol% CO_2, and balance N_2.

3. Results

3.1. Effect of sodium on the catalytic behavior

Figure 1 compares the NO conversion activity of iridium black samples with sodium contents amounting up to 10 at%. The absolute value for the maximum NO conversion showed slight variations between the different samples (ranging between 65 and 75%). Nevertheless, these deviations appear to be randomly distributed, and are hardly affected by the increase of the sodium content, covering a range of more than two orders of magnitude; it should be noted that at least part of these deviations may be ascribed to the rather large steps between each pair of temperature setpoints. For a more detailed investigation, the temperature levels for 20 (termed T_{onset}), and 50% NO conversion (relative to the maximum conversion) were determined and are listed in table 1. Even though the corresponding error bars must be assumed quite large (*ca.* ±10–15 °C), it is visible that higher sodium contents shift the NO conversion to higher temperatures by approximately 50 °C. Similar effects were also noticed for the parallel conversion of the reducing agents: the temperature at 50% conversion ($T_{50\%}$) was raised by about 15 °C for propene (∼235 to ∼250 °C; fig-

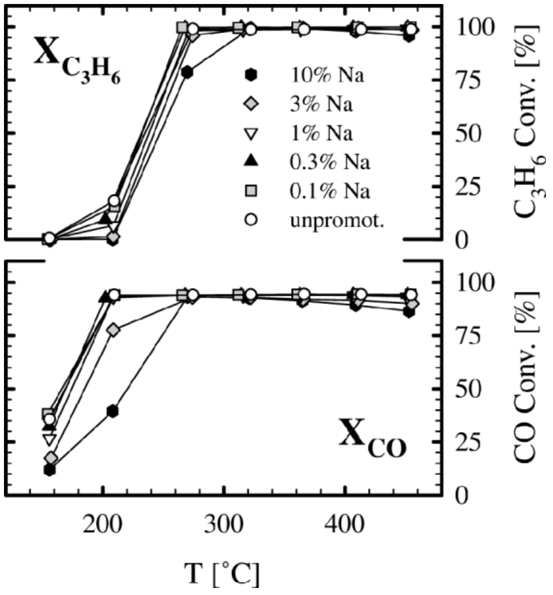

Figure 2. C_3H_6 (upper window) and CO conversion (lower window) over Ir black catalysts with different loadings of the sodium promoter as a function of temperature in a simulated exhaust gas mixture of 300 vpm NO, 0.18 vol% propene, 450 vpm CO, 8 vol% O_2, 10 vol% H_2O, 10.7 vol% CO_2, and balance N_2.

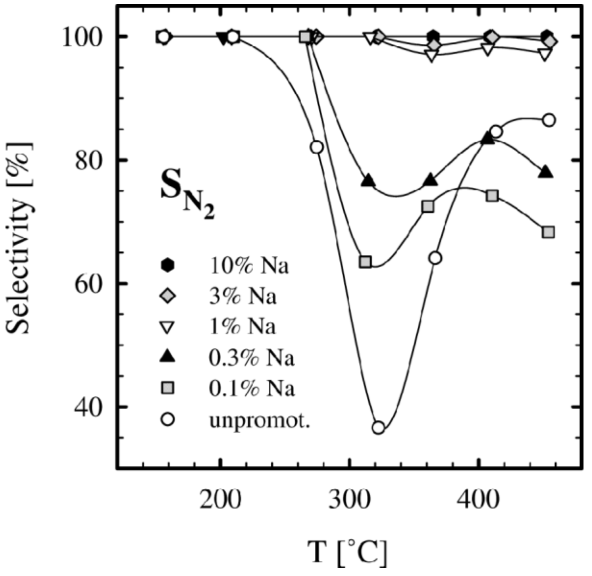

Figure 3. Nitrogen selectivity over Ir black catalysts with different loadings of the sodium promoter as a function of temperature in a simulated exhaust gas mixture of 300 vpm NO, 0.18 vol% propene, 450 vpm CO, 8 vol% O_2, 10 vol% H_2O, 10.7 vol% CO_2, and balance N_2.

ure 2, upper window) and by roughly 55 °C for CO (∼165 to ∼220 °C; figure 2, lower window), respectively. However, due to the extremely fast light-off for these reactions, the latter effects were solely visible for very high sodium loadings.

The corresponding nitrogen selectivities are displayed in figure 3. Here, the selectivity, is defined as

$$S_{N_2} = \frac{F^0_{NO} - F_{NO} - F_{NO_2}}{F^0_{NO} - F_{NO}} \times 100\%,$$

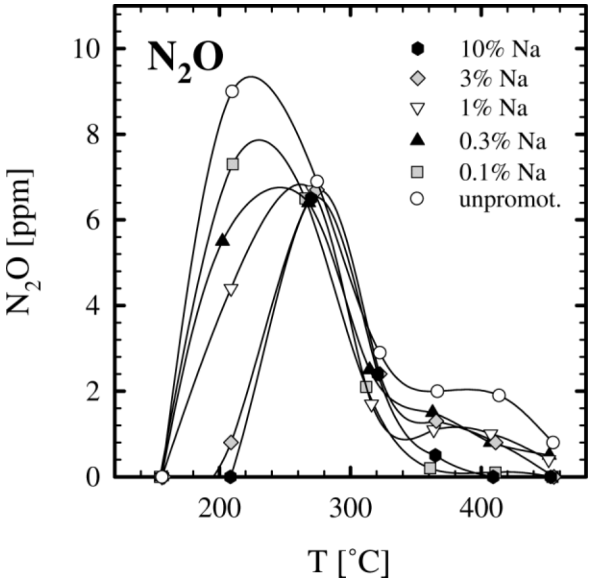

Figure 4. N_2O production over Ir black catalysts with different loadings of a sodium promoter as a function of temperature in a simulated exhaust gas mixture of 300 vpm NO, 0.18 vol% propene, 450 vpm CO, 8 vol% O_2, 10 vol% H_2O, 10.7 vol% CO_2, and balance N_2.

where F_i^0 is the flow of the corresponding component at the reactor inlet and F_i the flow at the outlet. Generally, increasing sodium contents led to a large increase of the selectivity up to an almost constant level of 100% for the highest promoter loadings, whereas on the unpromoted sample S_{N_2} dropped to a minimum of below 40% right after the on-set of the NO reduction.

At the highest temperatures measured, above 400 °C, however, selectivity decreased again slightly, with the unpromoted sample being the only exception. Even though for higher promoter loadings this effect was more and more covered by the strong, overall increase of selectivity, described above, it virtually affected all sodium-containing samples and therefore must be related to the presence of the promoter species. Note that at higher promoter loadings (>1 at% Na) the negative effect above 400 °C was almost completely compensated by the large, general increase in selectivity over the whole temperature range and therefore does not represent a significant drawback for a possible application in DeNO$_x$ catalysis.

The N_2O formation has not been included in the above selectivity calculations for the following reasons: (i) this reaction only occurs at temperatures of about 200–250 °C, below the on-set of the NO reduction to N_2, where the overall conversion is extremely small, (ii) the N_2O production rates are in general very small over iridium, hardly reaching the limit of quantification [7], and (iii) the latter rate strongly decreases with time on-stream, therefore not affecting the steady-state properties of iridium catalysts [8,9]. The observed traces of N_2O are displayed separately in figure 4. The data have been averaged over two independent runs in order to decrease the experimental error due to FTIR quantification methods. As was likewise observed for all other reactions, the on-set for N_2O formation shifted to higher

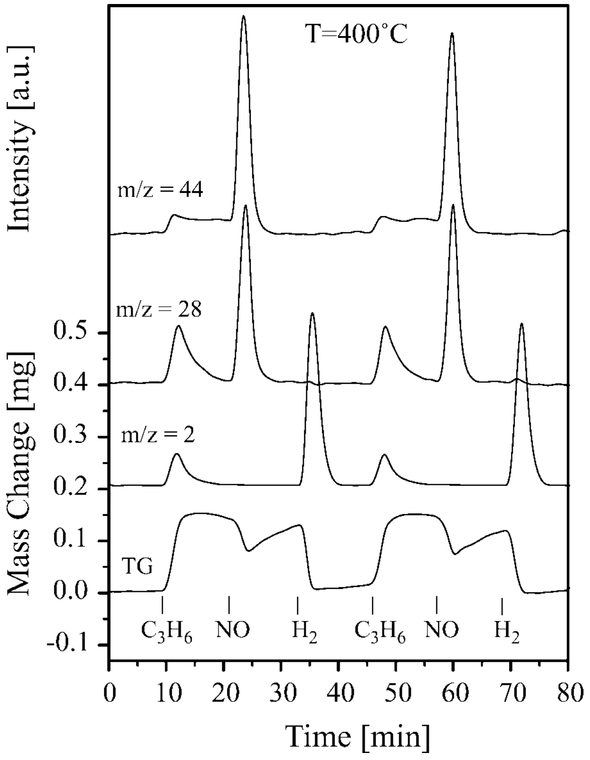

Figure 5. Change of mass and MS response on $m/z = 2$, 28, and 44 upon dosing first a pulse of propene and subsequently a pulse of NO, exemplary shown for the Ir black sample with 0.3 at% sodium. Finally, the original reduced state of iridium is restored by reduction with hydrogen.

temperatures for higher sodium loadings. The up-shift was accompanied by a decrease of the overall amount of N_2O produced (integrated area).

3.2. Effect of sodium on propene adsorption/decomposition

In preceding TG measurements it was observed that propene dissociates over iridium and gives rise to the formation of a carbonaceous deposit [8]. In the following, a series of different gas pulses was employed in order to compare quantitatively the amount of adsorbed C_xH_y species for the promoted iridium samples.

The change of mass and the corresponding response signals are exemplary shown for the sample with 0.3 at% sodium in figure 5. First a pulse of propene was introduced (volume of pulses is 1 cm^{-3}; $m_{\text{catalyst}} = 50$ mg; $T = 400\,^{\circ}\text{C}$), followed by a response on $m/z = 2$, resulting from hydrogen evolution after adsorption/dissociation. Subsequently pulsed NO oxidized iridium and reacted with the deposited carbon species, resulting in CO_2 ($m/z = 44$) and N_2 ($m/z = 28$) evolution. It was confirmed by parallel oxidation experiments that NO quantitatively removed all deposited carbon species. Finally, a hydrogen pulse reduced previously formed IrO_2 back into the metallic state. The sequence was repeated several times in order to check whether accumulation of any by-product species occurred – however, the latter could definitely be excluded.

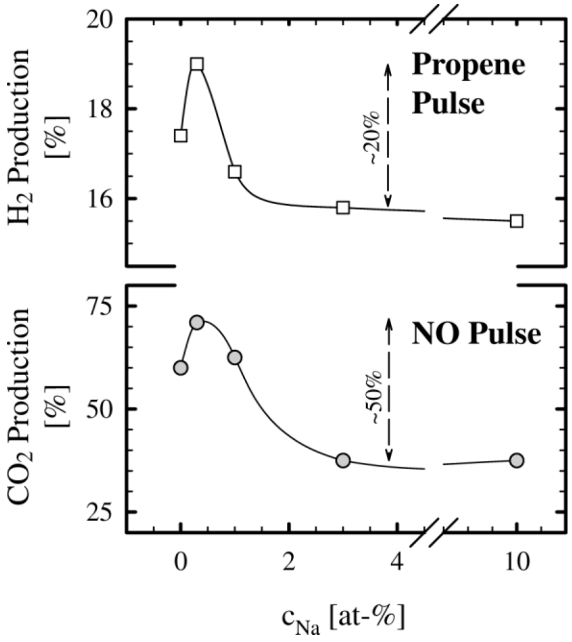

Figure 6. H_2 response upon dosing a pulse of propene over Ir black catalysts with different loadings of sodium (upper window) and CO_2 response after the subsequent reaction of the carbonaceous deposit with NO (lower window). The production of H_2 and CO_2 is given relative to the theoretical maximum amount. The explanation of the y-axis is given in the text. An example for the order of pulses in the experiment is provided in figure 5.

In figure 6 the hydrogen response (upper window), following the propene pulse, and the CO_2 response (lower window), caused by the NO reduction step, are compared for different sodium loadings (signals are corrected for background fragmentation of C_3H_6, contributing to the signal on $m/z = 2$). The y-axis for hydrogen production represents the ratio between the amount of hydrogen evolved during propene decomposition on the catalyst and the total amount of hydrogen in 1 cm^3 of C_3H_6 (*i.e.*, 3 cm^3 of hydrogen). The y-axis for CO_2 represents the ratio between the amount of CO_2 evolved due to a pulse of NO and the stoichiometric amount of CO_2 resulting from the reaction between carbonaceous deposits and NO. From 1 cm^3 NO 0.5 cm^3 CO_2 can be formed and this value is taken as 100%. It is evident that the presence of the promoter species strongly influences the adsorption/dissociation behavior of propene. Low sodium concentrations (0.3 at%) enhanced the decomposition of propene, as evidenced by the increase in H_2 and CO_2 production, respectively. For higher loadings (3 and 10 at%, respectively), however, the presence of sodium affected the amount of deposited C_xH_y species adversely.

It is noteworthy that the decrease at high promoter loadings occurred significantly larger in CO_2 production (*ca.* 50%) than in hydrogen formation (*ca.* 20%). A possible explanation for this dissimilarity could be the formation of adsorbed C_xH_y species with a higher hydrogen content. The fully quantitative comparison is, however, difficult due to low intensity of the recorded MS signals on $m/z = 2$.

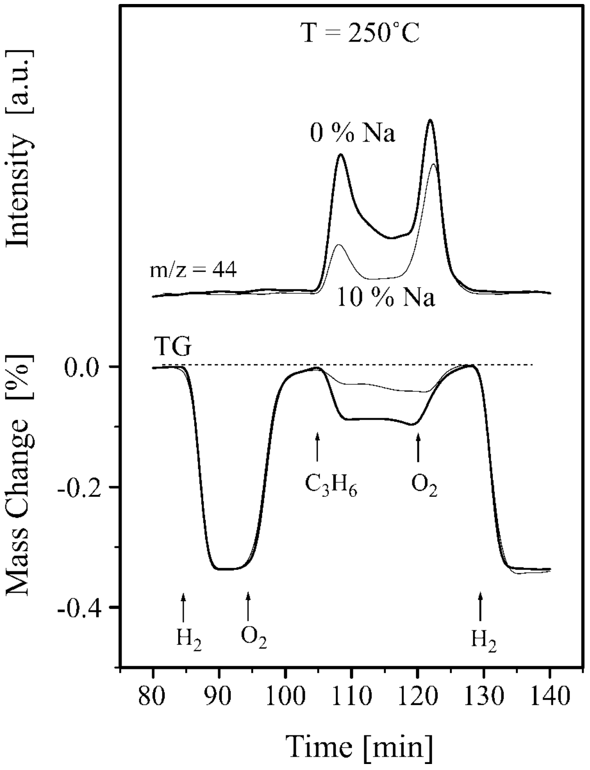

Figure 7. Change of mass and MS response on $m/z = 44$ upon dosing first a pulse of oxygen on the prereduced catalyst, followed by a pulse of propene. Subsequently, the carbonaceous deposit is removed by a second pulse of oxygen, and finally the adsorbed oxygen is reacted with hydrogen. The thick line corresponds to the unpromoted Ir black sample, while the thin line represents the sample with 10 at% sodium.

3.3. Effect of sodium on oxygen removal and iridium oxidation

It was found in preceding studies that the catalytic performance is governed by a subtle balance between metallic iridium and IrO_2 under DeNO$_x$ reaction conditions [7,9]. It is also known that alkali promoters strengthen the bonding of electronegative adsorbates, such as oxygen, to platinum metals (*e.g.* [18,19]).

Therefore, we first investigated the reactivity of preadsorbed oxygen towards pulses of propene by PulseTA. After reduction with hydrogen, oxygen was pulsed over the catalyst sample at 250 °C and subsequently reacted with a pulse of propene (figure 7). It is evident that on the sample containing 10 at% sodium a much smaller fraction of oxygen reacted than on the unpromoted sample, as was indicated by the smaller loss of mass due to the propene pulse and the reduced CO_2 evolution. Nevertheless, both catalysts had taken up the same amount of oxygen, as evidenced by the same weight uptake due to the oxygen pulse and confirmed by titration with hydrogen (figure 7).

After comparing the reactivity of the oxygen that was taken up by the catalyst samples, we additionally studied the ability of the different samples for iridium oxide formation by TG analysis. The different samples (*ca.* 50 mg) were heated up linearly (5 °C/min) in a stream of 20 vol% O_2, balance He (50 Nml/min). The corresponding weight increase due to oxidation is displayed in figure 8. Clearly, higher sodium loadings strongly promoted the oxidation of iridium at temperatures above 400 °C. Note that the oxidation is also affected by the crystallite size and sets in earlier for smaller crystallites, as were employed for the conversion experiments in this study. For illustration, figure 8 additionally presents the oxidation behavior of a 4 nm and of a 13 nm iridium black sample, respectively.

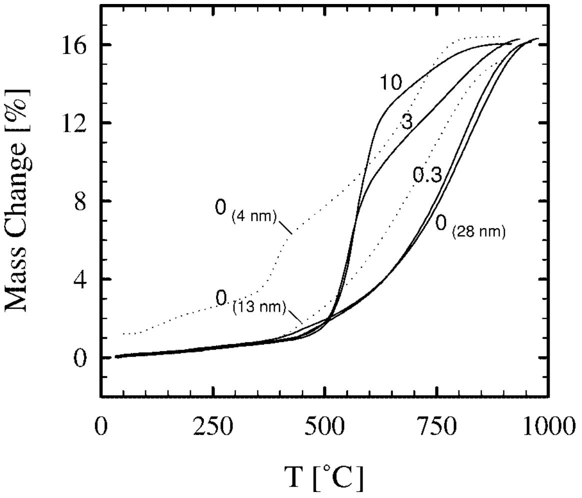

Figure 8. Oxidation of different pure and sodium-promoted Ir black samples, followed by TG in a stream of 20% O_2, balance He (10 °C/min).

The stronger bonding of oxygen to iridium and the enhanced formation of iridium oxide also caused changes in the facile Ir/IrO_2 equilibrium which is established under steady-state conditions during DeNO$_x$ reaction. Whereas the unpromoted sample showed a fraction of roughly 20% IrO_2 (determined by reduction with H_2 pulses after 12 h at 450 °C in the reaction mixture [8]), it was about 90% for the sample with 10 at% sodium.

4. Discussion

The activity measurements revealed that the presence of sodium does not enhance the activity of iridium black for NO reduction under the applied reaction conditions. Each sample reached a similar high level of maximum NO conversion.

It may be noticed that at least for the sample with the highest loading a significant fraction of the iridium surface must be physically covered by sodium carbonate. The still high activity of this catalyst implies that only part of the surface is involved in the reaction process and that these specific sites are not blocked by the sodium carbonate. Similar effects have been observed by Konsolakis *et al.* or Yentekakis *et al.* for Pt/Al_2O_3, where the activity (and nitrogen selectivity) of samples with an almost fifty-fold excess of Na (in at%) was still comparable to those with lower Na loadings [13,20]. However, in the latter case an unknown, but significant fraction of the promoter species was also located on the support, which handicaps a direct comparison to our unsupported catalyst.

Although the observed effect was relatively small, it is apparent that sodium shifted the on-set of all participating reactions to higher temperatures, thus cutting the lower limit of the operation temperature window. The latter represents a considerable drawback for a possible application in $DeNO_x$ catalysis, since in general a larger temperature window is desired, especially on the low temperature side with view on the cold-start properties [1].

The observed effects of sodium on the activity are in-line with results on the propene conversion over alkali-promoted Pd/Al_2O_3, reported by Shinjoh *et al.* [16], but clearly differ from those of a very similar study on sodium promotion for a Pt/Al_2O_3 catalyst, published recently by Konsolakis *et al.* [13]. There, the temperature levels for 50% conversion of NO, CO, and propene had been lowered by ∼70–95 °C at optimum promoter loading. Although part of this discrepancy may be attributed to the different nature of the employed noble metals, we predominantly ascribe it to the differing reactant feed gas compositions, in particular to the large oxygen excess in our simulated exhaust gas ($NO:O_2 = 1:27$ *vs.* $1:8$ in the study by Konsolakis *et al.* [13]). Such high oxygen contents were previously found to be detrimental to the positive effect of sodium on the activity which was noticed over Pt/Al_2O_3 [21].

The selectivity, however, was strongly improved by the presence of sodium, resulting from a significant suppression of the unfavorable NO_2 formation. This corresponds very well to recent results on Pt/Al_2O_3 [13,20] or Pd/ZrO_2 [14], where a distinct enhancement of the nitrogen selectivity has been reported after impregnation with sodium nitrate. Consequently, other than for the above discussed effect on the activity, the effect on the selectivity appears to be little influenced by the differences in the feed gas composition. Mechanistically, the increased selectivity was explained in the literature by an increased adsorption energy of NO on the metal in the presence of alkali adatoms, which is accompanied by a lowering of the N–O bond strength, resulting from an enhanced population of the NO π^*-orbital [20,22,23]. The latter would facilitate the NO dissociation

$$NO_{ad} \rightleftharpoons N_{ad} + O_{ad} \qquad (1)$$

and result in a higher θ_N *vs.* θ_{NO} ratio. Hence N_2 formation

$$2N_{ad} \rightleftharpoons N_2 \qquad (2)$$

becomes more favorable at the expense of the NO_2 or N_2O production,

$$NO_{ad} + O_{ad} \rightleftharpoons NO_2 \qquad (3)$$

$$NO_{ad} + N_{ad} \rightleftharpoons N_2O \qquad (4)$$

It cannot be excluded, however, that other effects, such as the observed alteration of the oxidation behavior for iridium, additionally contribute to the observed selectivity increase at larger sodium loadings.

Presumed that the NO reduction proceeds predominantly *via* the “dissociation model” (equations (1) and (2)), as was proposed by several authors [2,24–26], in principle three reaction steps appear likely to be limiting to the overall process, since they are known to be governed by relatively high activation barriers. First, removal of chemisorbed oxygen [27], second, removal of adsorbed propene fragments (or of possible oxygenated species [28]) [21], and finally, dissociation of nitric oxide [29]. The fact that on iridium, other than reported for supported Pt and Pd catalysts [13,14], the enhanced selectivity was not accompanied by a parallel increase of the NO reduction implies that under our reaction conditions NO dissociation does not represent the rate-determining step for the $DeNO_x$ process, as was proposed for the other platinum metals under the corresponding conditions (*e.g.* [13,20,30]). TG-MS results revealed the build-up of a carbonaceous deposit on iridium after dosing propene. The amount of the deposit was shown to critically depend upon the sodium content and, according to the CO_2 response, varied by a factor of *ca.* 2 for the different samples. But neither activity nor selectivity showed any analogous dependencies, therefore the deposition and/or removal of such species is not likely to be decisive for the NO reduction process. The reactivity of adsorbed oxygen (determined *via* its reaction with propene) and the subsequent oxidation of iridium, however, were strongly influenced at higher sodium loadings. Increased site-blocking by adsorbed oxygen may well explain the observed continuous up-shift of the on-set temperature for all participating reactions. Such a surface, covered predominantly by oxygen under our reaction conditions, seems likely due to the high oxygen content of the employed feed gas. In view of the complexity of the feed gas composition and of the overall reaction process, however, the latter implications are rather speculative. To prove the suggested reaction mechanism detailed kinetic measurements are needed. This will be subject to further investigations.

5. Conclusions

The impregnation of iridium catalysts with sodium carbonate was demonstrated to be a very effective way for improving the nitrogen selectivity in the HC-SCR reaction close to 100% in a simulated lean exhaust gas mixture. Due to a small detrimental effect on the activity (narrowing of the operation temperature window), counteracting the benefits from the increased selectivity, moderate sodium loadings in the range of 1–3 at% represent the best compromise. Mechanistically, our results are consistent with a model where NO dissociation is not rate-limiting, as was proposed earlier for supported Pt and Pd catalysts (*e.g.* [15,25]). Instead, the removal of adsorbed oxygen, which is further impeded by the presence of sodium, is likely to be the decisive step under the applied reaction conditions.

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References

[1] H. Akama and K. Matsushita, Catal. Surv. Jpn. 3 (1999) 139.

[2] R. Burch and P.J. Millington, Catal. Today 26 (1995) 185.

[3] R.J. Farrauto and R.M. Heck, Catal. Today 51 (1999) 351.

[4] V.I. Parvulescu, P. Grange and B. Delmon, Catal. Today 46 (1998) 253.

[5] M. Nawdali, H. Praliaud and M. Primet, in: *Prepr. of 5th Int. Congr. on Catalysis and Automotive Pollution Control*, eds. N. Kruse, A. Frennet and J.-M. Bastin (ULB, Brussels, 2000) p. 107.

[6] T. Nakatsuji, Appl. Catal. B 25 (2000) 163.

[7] C. Wögerbauer, M. Maciejewski, A. Baiker and U. Göbel, in: *Prepr. of 5th Int. Congr. on Catalysis and Automotive Pollution Control*, eds. N. Kruse, A. Frennet and J.-M. Bastin (ULB, Brussels, 2000) p. 203.

[8] C. Wögerbauer, M. Maciejewski and A. Baiker, submitted for publication.

[9] C. Wögerbauer, M. Maciejewski, A. Baiker and U. Göbel, J. Catal., in press.

[10] F. Radtke, R.A. Köppel and A. Baiker, Catal. Today 26 (1995) 159.

[11] F. Radtke, R.A. Köppel, E. Minardi and A. Baiker, J. Catal. 167 (1997) 127.

[12] R. Willi, R.A. Köppel and A. Baiker, Ind. Eng. Chem. Res. 36 (1997) 3013.

[13] M. Konsolakis, N. Macleod, J. Isaac, I.V. Yentekakis and R.M. Lambert, J. Catal. 193 (2000) 330.

[14] I.V. Yentekakis, R.M. Lambert, M.S. Tikhov, M. Konsolakis and V. Kiousis, J. Catal. 176 (1998) 82.

[15] R. Burch and T.C. Watling, Appl. Catal. B 11 (1997) 207.

[16] H. Shinjoh, N. Isomura, H. Sobukawa and M. Sugiura, Stud. Surf. Sci. Catal. 116 (1998) 83.

[17] M. Maciejewski, C.A. Müller, R. Tschan, W.-D. Emmerich and A. Baiker, Thermochim. Acta 295 (1997) 167.

[18] I.V. Yentekakis, A. Palermo, N.C. Filkin, M.S. Tikhov and R.M. Lambert, J. Phys. Chem. B 101 (1997) 3759.

[19] G. Pirug, H.P. Bonzel and G. Broden, Surf. Sci. 122 (1982) 1.

[20] I.V. Yentekakis, M. Konsolakis, R.M. Lambert, N. Macleod and L. Nalbantian, Appl. Catal. 22 (1999) 123.

[21] N.C. Filkin, M.S. Tikhov, A. Palermo and R.M. Lambert, J. Phys. Chem. 103 (1999) 2680.

[22] N.D. Lang, S. Holloway and J.K. Nørskov, Surf. Sci. 150 (1985) 24.

[23] I.R. Harkness and R.M. Lambert, J. Chem. Soc. Faraday Trans. 93 (1997) 1425.

[24] V.V. Savkin and M.U. Kislyuk, Kinet. Katal. 37 (1996) 555.

[25] I.V. Yentekakis, A. Palermo, M.S. Tikhov, N.C. Filkin and R.M. Lambert, Stud. Surf. Sci. Catal. 116 (1998) 255.

[26] B.A. Banse, D.T. Wickham and B.E. Koel, J. Catal. 119 (1989) 238.

[27] C.-B. Wang, J.-G. Chang, R.-C. Wu and C.-T. Yeh, Appl. Catal. B 17 (1998) 51.

[28] A. Obuchi, M. Nakamura, A. Ogata, K. Mizuno and H. Ohuchi, Appl. Catal. B 2 (1993) 71.

[29] R.-J. Wu and C.-T. Yeh, Int. J. Chem. Kinet. 28 (1996) 89.

[30] R. Burch, Catal. Today 35 (1997) 27.