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A Kinetic and Spectroscopic Study of the *in Situ* Electrochemical Promotion by Sodium of the Platinum-Catalyzed Combustion of Propene

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The electrochemical promotion (EP) of propene combustion has been studied over a platinum film catalyst supported on sodium β''-alumina. Fully reversible promotion and poisoning are observed as a function of catalyst potential (i.e., sodium coverage), the precise behavior being dependent on reactant partial pressures. A model based on a Langmuir−Hinshelwood mechanism and Na-modified chemisorption of the reactants accounts for all the results: Na enhances the chemisorption of oxygen and inhibits the chemisorption of propene. The formation, chemical identity, stability, and electrochemical decomposition of the Na surface compounds produced in the promoted and poisoned regimes were explored using postreaction XPS, AES, and, for the first time, postreaction Na K edge XAFS. These results indicate that thick layers consisting of sodium carbonate are responsible for catalyst poisoning. The promoter phase consists of smaller amounts of sodium carbonate, and much of this material is present as three-dimensional crystallites. These promoter and poisoning phases are stable at reaction temperature, but rapidly destroyed by electropumping Na away from the catalyst surface. Their direct participation in the electrochemically promoted reaction is thereby demonstrated.

Introduction

Electrochemical promotion (EP) entails electropumping of ions from a solid electrolyte to the surface of a porous, catalytically active metal film where they alter the catalytic properties of the latter.[1] These spilt-over promoter species induce changes in catalyst potential over a range of ~1 V measured with respect to a reference electrode (ΔV_{WR}) which are closely related to the change in catalyst work function. The resulting changes in adsorption enthalpies and reaction activation energies can lead to major changes in catalytic activity and selectivity. The effects on activity and selectivity are generally reversible, and the phenomenon provides an effective method for the in situ tuning of working catalytic systems.

EP of ethene combustion over metal film catalysts supported on a variety of solid electrolytres has been reported previously. For Pt films supported on both Na−β''-alumina (a Na^+ conductor)[2,3] and yttria stabilized zirconia (YSZ; an O^{2-} conductor),[4] promotion occurs as the catalyst potential *decreases*, though only under fuel-rich conditions. Furthermore, in the former case poisoning was observed at sufficiently negative catalyst potentials (high Na loadings).[2,3] Model studies on the Na/Pt(111) system suggest that this poisoning is due to formation of a surface alkali metal carbonate.[5] A limited EP study of propene combustion has been reported, using Pt supported on YSZ.[6] However in this case, *increasing* the catalyst potential under fuel-lean conditions led to rate enhancement. There have been no previous EP studies of propene combustion by sodium.

Our earlier work[7] on the EP by Na of the Pt-catalyzed reduction of NO by propene achieved three ends. First, it shed light on the reaction mechanism and on the role of Na promoter in accelerating the process. Second, it showed what the chemical state of the Na promoter phase actually is under reaction conditions. Third, it prompted the successful development of highly active, Na-promoted, conventional dispersed catalysts for the NO + propene reaction.[8] We showed[7] that with increasing Na loading, a regime of very strong electrochemical promotion (of both overall activity and selectivity toward N_2 formation) was followed by a regime of strong poisoning. XP spectra revealed that under reaction conditions the promoter phase consisted of a mixture of sodium nitrite and sodium nitrate, and that the promoted and poisoned conditions of the catalyst correspond to low and very high loadings of these sodium compounds. Promotion of both activity and N_2 selectivity was ascribed to Na-induced dissociative chemisorption of NO, a proposal that is supported by recent Monte Carlo simulations.[9]

Here, we seek to make a corresponding contribution in regard to the O_2 + propene reaction. Promoted and poisoned regimes are again observed, but the behavior is markedly different from that of the propene + NO system. Together, these two sets of results provide the necessary background against which subsequent EP studies of NO reduction by propene in an oxygen-rich environment can be undertaken.

Experimental Methods

The preparation and operation of the EP Pt/β''-alumina sample, and the design and performance characteristics of the EP reactor and of the laboratory XPS analysis system have been described in detail elsewhere.[7] A concise summary follows. The EP catalyst sample consisted of a wafer of Na−β''-alumina (~15 × 10 × 1.5 mm) onto which a platinum catalyst working electrode was deposited. Gold counter and reference electrodes were evaporated in vacuo onto the reverse side of the wafer and all gas-exposed electrical connections to the sample were made using gold wire; control experiments showed that the gold

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components were catalytically inert under our conditions. The catalyst surface area was 4.5×10^{-7} mol of Pt atoms,[7] and electrochemical control of the sample was achieved using an AMEL 553 potentiostat−galvanostat.

Reaction studies were carried out using an atmospheric pressure well-mixed flow reactor,[7] quantitative analysis of reactants and products being achieved by gas chromatography (Porapak N and molecular sieve 5A columns) and quadrupole mass spectrometry. Reactants were fed by mixing 20% oxygen in He and 5% propene in He with pure helium by means of electronic mass flow controllers. Partial pressures were 0−0.8 kPa (propene) and 0−7 kPa (oxygen), and total flow rates of 2×10^{-4} mol s^{-1} (270 cm^3 min^{-1} STP) were employed.

X-ray photoelectron spectra were acquired with a VG ADES 400 system, base pressure 10^{-10} Torr, using Mg Kα radiation. The sample was mounted on a ceramic block using gold electrical connections and heated via embedded tungsten filaments. This assembly could be translated via a gate valve between the ultra-high-vacuum (UHV) XPS chamber and a controlled environment cell. Postreaction XP spectra were acquired using the cell as a batch reactor while maintaining UHV in the main chamber. The procedure was as follows: (i) sample held at constant temperature and catalyst potential in the reaction cell in high vacuum; (ii) pure reactants at appropriate partial pressures plus nitrogen admitted to a total pressure of 1 atm, thus fully simulating conditions used in the reactor studies; (iii) sample cooled, reaction cell evacuated, electrochemical bias removed; (iv) transfer to XPS chamber for examination. The design of the sample holder and transfer probe also allowed electrochemical biasing and heating of the sample *during acquisition of XP spectra*. All XPS measurements were carried out with the platinum working electrode (i.e., the catalyst film) at ground potential. Quoted binding energies are referenced to the Au $4f_{7/2}$ emission at 83.8 eV, this emission arising from the Au connections to the Pt working electrode. In these experiments, sample conditioning in reaction gas and subsequent XPS data acquisition were carried out at 588 K rather than at 613 K (the temperature used in the reactor). This reflects limitations of the XPS sample holder; however, the 25 K difference seems unlikely to cause major discrepancies between the reactor and XPS results.

Postreaction X-ray absorption spectra at the Na K edge were acquired using beamline 3.4 of the Daresbury Laboratory Synchrotron Radiation Source. The apparatus consisted of a small cell (∼100 cm^3) allowing gas exposure of a heated and electrochemically biased sample under gas flow conditions at atmospheric pressure, followed by pump down and transfer of the sample into the high-vacuum chamber on the beamline. Data were recorded in total electron yield mode, using a collector placed approximately 50 mm from the sample and connected to ground via a current amplifier, with the catalyst film biased at −100 V with respect to ground. XAS data were acquired from the quenched sample, i.e., at room temperature and in the absence of applied potentials between working and counter electrodes. Appropriate standard spectra were also acquired using relevant pure compounds that were ground finely, mixed with graphite powder to provide electrical conductivity, and compressed to a 1 mm thick × 10 mm diameter wafer.

Results

Microreactor Studies. Figure 1 shows the effect on steady-state CO_2 production rate of varying the catalyst potential (V_{WR}) in reactant feeds with three different reactant partial pressure ratios ($P_{oxygen}/P_{propene} = 2-5.7$) at constant total flow rate. At high positive potentials, ∼+1 V, the platinum surface is electrochemically cleaned and should be Na-free (see below). It can be seen that the reaction rate on this clean Pt surface (r_0) scales approximately linearly with oxygen pressure. As V_{WR} is decreased below ∼+400 mV, Na is supplied electrochemically to the platinum working electrode and the rate of CO_2 production increases, to varying degrees. We refer to this as the promoted regime: the estimated coverage of the Na promoter phase is in the submonolayer range (see below). As V_{WR} is reduced further, more Na is supplied to the catalyst surface and the rates exhibit maxima (r_{max}), eventually falling off as V_{WR} is decreased below ∼ −300 mV. We refer to the latter as the poisoned regime: it corresponds to growth of three-dimensional crystallites of Na compounds on the Pt surface (see below). The ratio r_{max}/r_0 of the optimally promoted rate to the clean surface rate is also indicated in Figure 1, for each case. As $P_{oxygen}/P_{propene}$ *decreases*, the effects of Na promotion increase rapidly. Thus for $P_{oxygen}/P_{propene} = 5.7$, where overall activity is highest, $r_{max}/r_0 = 1.1$, after which it *increases* to 2.3 at $P_{oxygen}/P_{propene} = 2.0$, where overall activity is lowest. In other words, these results suggest that the order in propene is negative, and that Na accelerates the rate by decreasing self-poisoning due to propene; all the remaining reactor data are consistent with this view.

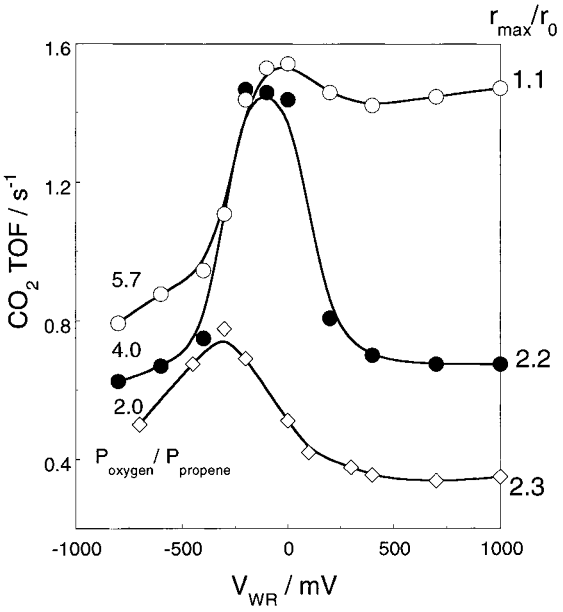

Figure 1. Effect of catalyst potential V_{WR} on CO_2 production rate, at various reactant partial pressures. Conditions: $T = 613$ K, $F_T = 300$ cm^3 min^{-1}.

Accurate measurement of the water production rate was not possible due to partial condensation within the sampling system; however, the behavior of the H_2O rate was qualitatively the same as that for CO_2 production under all conditions. No CO production was observed and the carbon mass balance closed to within 3%.

Figures 2 and 3 show the effect on reaction rate of varying the partial pressure of propene and oxygen, respectively, at constant outlet partial pressure of the other reactant, for three different values of V_{WR} (+500, 0, −600 mV). As is apparent from Figure 1, these three values of catalyst potential correspond to Na-free, promoted, and poisoned surfaces, respectively. In these experiments, conversion of reactants was kept below 20% to avoid mass transfer limitations. At $V_{WR} = +500$ mV, (i.e., on the Na-free catalyst) the rate shows a very pronounced maximum as a function of propene partial pressure (Figure 2). In the promoted regime ($V_{WR} = 0$ mV) the maximum is less

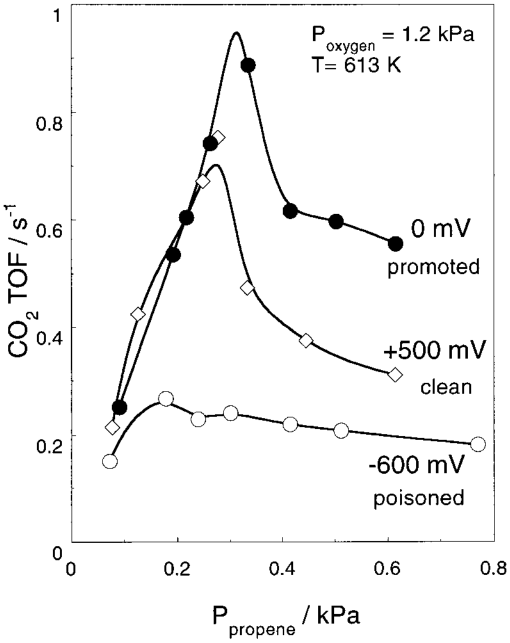

Figure 2. Dependence of reaction rate on propene partial pressure for unpromoted, promoted, and poisoned surfaces. Conditions: $P_{\mathrm{O_2}} = 1.2$ kPa, T =613 K, $F_{\mathrm{T}} = 300$ cm^3 min^{-1}.

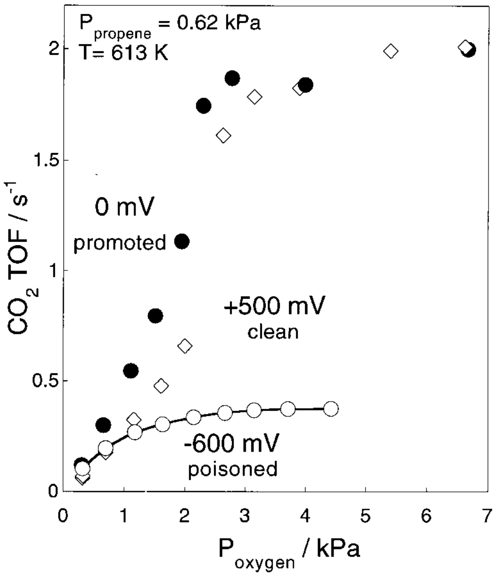

Figure 3. Dependence of reaction rate on oxygen partial pressure for unpromoted, promoted, and poisoned surfaces. Conditions: $P_{\mathrm{C_3H_6}} =$ 0.62 kPa, $T = 613$ K, $F_{\mathrm{T}} = 300$ cm^3 min^{-1}.

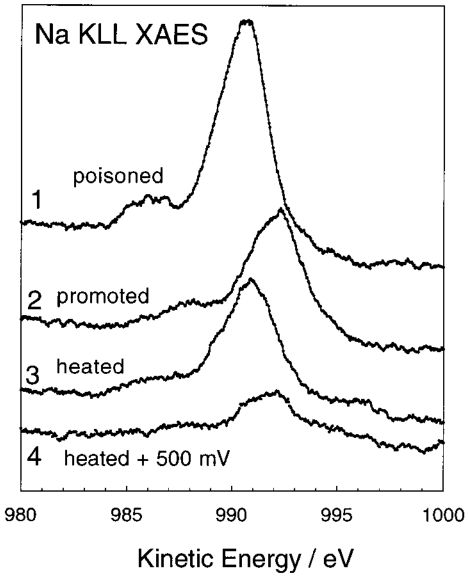

Figure 4. Sodium KLL XAE spectra taken after catalyst exposure to 0.6 kPa of propene and 2.5 kPa of oxygen, at 588 K; all spectra acquired at room temperature, open circuit, after subjecting sample to specified conditions. 1, poisoned conditions,$V_{\mathrm{WR}} = -600$ mV; 2, promoted conditions, $V_{\mathrm{WR}} = -100$ mV; 3, as 2 but after heating to 588 K; 4, as 3 but after imposing $V_{\mathrm{WR}} = +500$ mV.

pronounced. The maximum rate is *shifted to higher propene pressure relative to the unpromoted case.* In the poisoned regime ($V_{\mathrm{WR}} = -600$ mV) activity is of course strongly suppressed at all propene pressures and no maximum is discernible.

The results illustrated in Figure 2 suggest competitive adsorption of the two reactants on the catalyst surface. The corresponding results for the rate as a function of oxygen pressure at fixed propene pressure are shown in Figure 3: in this case, rate maxima are not observed within the range of accessible oxygen pressures.

X-ray Photoelectron Spectroscopy. In interpreting these results, it should be borne in mind that the Pt film is continuous though porous, so that the underlying Na$-\beta''$-alumina is line-of-sight spectroscopically visible through cracks and imperfections in the metal deposit.[7] As we have shown,[7] photoemission from species present on the (grounded) Pt film is distinguishable from that arising from the underlying β''-alumina. Thus as V_{WR} is varied the electron binding energy (BE) of (say) a given sodium or oxygen species on the Pt remains invariant, whereas the apparent BEs of Na and oxygen atoms in the solid electrolyte varies by an amount exactly equal to the change in V_{WR}.

XP spectra were obtained immediately after exposing the appropriately biased catalyst film to the *conditions of temperature and reactant partial pressures typical of those encountered in the reactor,* in order to simulate as closely as possible the various surface conditions of interest. The reactant partial pressures used correspond to the region in the middle of Figure 3, where there are major differences in catalytic behavior between the promoted and poisoned cases. During exposure of the catalyst to the reaction gas mixture, the V_{WR} values were such that the Pt film was either (i) electrochemically clean, (ii) promoted, or (iii) poisoned. Spectra were acquired after a pump-down period of ~2 h, the sample temperature being lowered to ~420 K before pump down and the imposed bias (V_{WC}) between catalyst and counter electrode switched off when the sample temperature was <450 K; i.e., the system was switched to open circuit conditions when Na mobility was low. This procedure was designed to “freeze”, insofar as possible, the surface conditions prevailing in the reactor, at temperature and pressure and under conditions of electrochemical bias.

Figure 5 shows Na 1s XP spectra from poisoned (spectrum 1), promoted (spectrum 2), and electrochemically cleaned (spectrum 3) surfaces. Spectra were acquired after exposing the sample to a mixture of 0.6 kPa of propene + 2.5 kPa of O_2 at 588 K, following the procedure described above. Reaction gas exposure was carried out under two sets of conditions: (i) with $V_{\mathrm{WR}} = -600$ mV (poisoned catalyst) and (ii) with $V_{\mathrm{WR}} = -100$ mV (promoted catalyst). It can be seen that, within the sampling depth of the technique (~5 Å, photoelectron kinetic energy 180 eV), a similar amount of Na is detected on the poisoned and promoted catalysts. Heating the poisoned and promoted surfaces to 588 K produced no detectable changes (spectra not shown), but electrochemical cleaning ($V_{\mathrm{WR}} = +500$ mV at 588 K) caused a substantial decrease in the Na signal intensity (spectrum

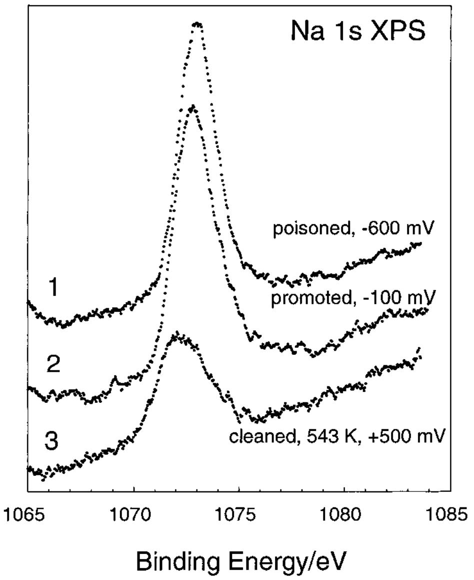

Figure 5. Sodium 1s XP spectra taken after catalyst exposure to 0.6 kPa of propene and 2.5 kPa of oxygen, at 588 K; all spectra acquired at room temperature, open circuit, after subjecting sample to specified conditions. 1, poisoned conditions, $V_{WR} = -600$ mV; 2, promoted conditions, $V_{WR} = -100$ mV; 3, as 1, after heating to 588 K and imposing $V_{WR} = +500$ mV.

3). Note that the residual Na 1s peak shows a lower BE (1072.5 eV): this has been shown[7] to be due to Na in the underlying β''-alumina electrolyte, visible through cracks and imperfections in the Pt film.

Figure 4 shows corresponding Na KLL Auger spectra from poisoned (spectrum 1), promoted (spectrum 2), promoted, then heated (spectrum 3), and electrochemically cleaned (spectrum 4) surfaces. The electron kinetic energy in this case is 990 eV, corresponding to a sampling depth of ~15 Å. A clear difference is now apparent between the poisoned and promoted cases with respect to both peak position and peak intensity. Heating the promoted surface leads to a shift in Na KLL kinetic energy back toward the poisoned value (5.3), and electrochemical cleaning of the Pt leaves only the emission from the underlying β''-alumina[7] (5.4). Note that during electrochemical cleaning of the poisoned surfaces a rise in pressure occurred in the vacuum system, signifying release of gaseous species during electrodecomposition of the poisoning phase. This is certainly significant, althougn our apparatus did not allow us to identify the gas released.

XP spectra of the Pt 4f doublet at 71.0 and 74.5 eV are shown in Figure 6. Spectrum 1 refers to the poisoned surface. Note the almost complete attenuation of Pt emission due to Na compounds covering the catalyst surface; this corresponds to the presence of a layer ~40−50 Å thick of the poisoning compound. In this case the amount of Na present is sufficiently large for the Na 2s emission to be clearly visible at 64.2 eV. The residual emission in the Pt 4f region is Al 2p from the (uncovered) solid electrolyte. Spectrum 2 refers to the promoted surface. Clearly, there is substantially less attenuation of Pt emission by surface compounds of Na in this case: it corresponds to a uniform film of ~7−10 Å thickness. Spectrum 3 refers to the clean surface. It was acquired after heating and electrochemically cleaning the poisoned surface. The small peaks at 62.5 and 66.0 eV are Pt 4f satellites due to the Mg $K\alpha_2$ line from the X-ray source.

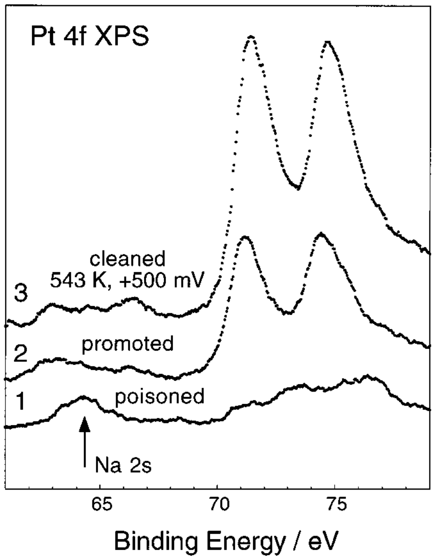

Figure 6. Platinum 4f XP spectra. 1, poisoned conditions, $V_{WR} = -600$ mV; 2, promoted conditions, $V_{WR} = -100$ mV; 3, as 1, after heating to 588 K and imposing $V_{WR} = +500$ mV; other conditions as in Figures 4 and 5.

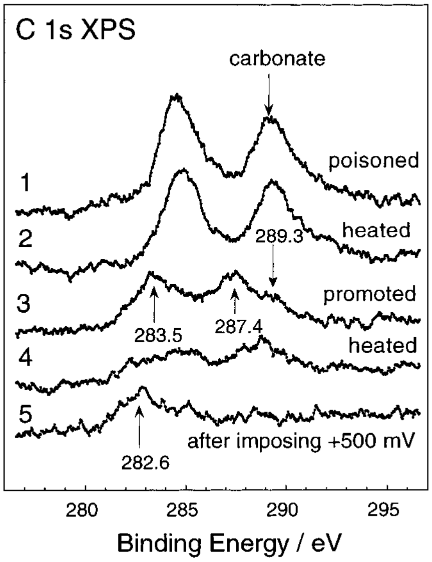

Figure 7. (i) Carbon 1s XP spectra. 1, poisoned conditions, $V_{WR} = -600$ mV; 2, poisoned conditions after heating to 588 K; 3, promoted conditions, $V_{WR} = -100$ mV; 4, promoted conditions after heating to 588 K; 5, as 4 after imposing $V_{WR} = +500$ mV; other conditions as Figures 4 and 5.

Carbon 1s XP spectra provide some evidence about the chemical identity of the Na compounds that are formed under reaction conditions (Figure 7). These data suggest that, after exposure to reaction conditions, Na is present as a carbon-containing compound or compounds. If this is correct, they also confirm that the poisoned surface carries substantially more Na compound(s) than the promoted surface (spectrum 1 versus spectrum 3). The poisoned surface exhibits two distinct C 1s features at 284.6 and 289.5 eV, and heating to 588 K results in little change. The promoted surface (spectrum 3) exhibits peaks at 283.5 and 287.4 eV with shoulders at 286.0 and 289.5 eV. In this case, heating to 588 K *does* attenuate the C 1s spectrum, yielding spectrum 4. Finally electrochemical cleaning leaves a single peak at 282.6 eV which we assign to a small amount of carbidic carbon, probably resulting from the calcination procedure used in Pt film preparation (spectrum 5).

The oxygen 1s XP spectra (Figure 8) also show changes in the nature of the surface compounds present as the catalyst was

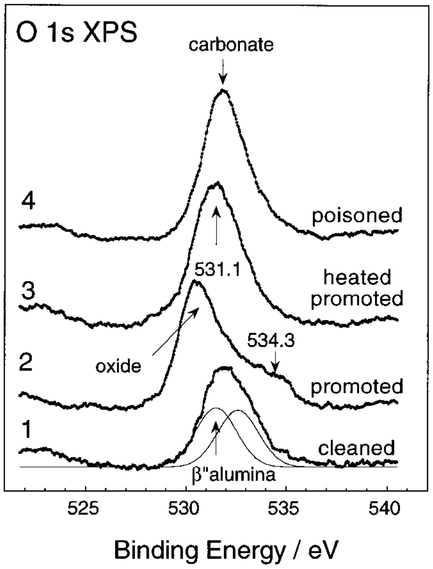

Figure 8. Oxygen 1s XP spectra. 1, electrochemically cleaned showing contribution from β''-alumina; 2, promoted conditions, $V_{WR} = -100$ mV; 3, as 2, heated to 588 K; 4, poisoned conditions, $V_{WR} = -600$ mV.

subjected to larger or smaller Na loadings, heating, and electrochemical cleaning. Spectrum 1 corresponds to the poisoned surface, spectrum 3 to promoted conditions. Heating the promoted surface produces spectrum 2, and electrochemical cleaning (+500 mV; 588 K) of either the promoted or poisoned surfaces leads to spectrum 4. In spectrum 4 we have indicated the separate contributions from the β''-alumina (see above) and from a residual oxygen species, apparently on the Pt surface.

X-ray Absorption Near Edge Structure (XANES). This is the first study in which postreaction XANES has been used to study an electrochemically promoted catalyst. The objective was to obtain additional information about the chemical state of the catalyst surface in the promoted and poisoned regimes. Figure 9a shows Na K edge XANES postreaction data taken after subjecting the catalyst sample to promotion or poisoning in the environmental cell immediately before sample transfer and spectral acquisition. The conditions used were as follows: poisoned regime, $V_{WR} = -600$ mV, $P_{propene} = 0.4$ kPa, $P_{O_2} = 1.6$ kPa; promoted regime, $V_{WR} = -100$ mV, $P_{propene} = 0.2$ kPa, $P_{O_2} = 0.8$ kPa. In both cases $P_{total} = 1$ atm (balance N_2), $F_T = 250$ cm^3 min^{-1}, $T = 565$ K. A current transient between the counter and working electrodes was observed when the gases were introduced under poisoning conditions (i.e., V_{WR} held at -600 mV): a spike of ~ -10 mA was followed by an exponential decrease to ~200 μA for the following 1−2 min. This indicates electrochemical supply of a large amount of Na to the catalyst. From the known Pt film surface area[7] we may estimate that this corresponds to delivering an amount of Na equivalent to a uniform coverage of ~100 monolayers. For the promoted regime the corresponding transient gave a spike of ~ -250 μA, followed by exponential decay, corresponding to a uniform coverage by the promoter phase in the order of 13 monolayers.

Figure 9a also shows a clean surface spectrum, along with reference spectra obtained using sodium carbonate and sodium hydrogen carbonate. Note that the height of the sodium edge jump has not been normalized, so it is indicative of the relative amounts of sodium detected in the various samples. Clearly, the amount of sodium is much larger in the poisoned case than in the promoted and clean surface cases, in agreement with the laboratory XPS data. The clean surface residual spectrum is assigned to Na in the underlying β''-alumina, consistent with the porosity of the Pt film. It is apparent that the spectrum from the poisoned surface is closely similar to that of bulk sodium carbonate. The derivatives of the "poisoned" and of the Na_2CO_3 reference spectra are presented in Figure 9b: the close agreement suggests strongly that the poisoned surface is indeed covered by sodium carbonate.

Discussion

Figure 1 shows that the effectiveness of electrochemical promotion (as judged by the ratio of the maximum promoted rate to the unpromoted rate: r_{max}/r_0) is strongly dependent on gas-phase composition. Under oxygen-rich conditions, (P_{O_2}/

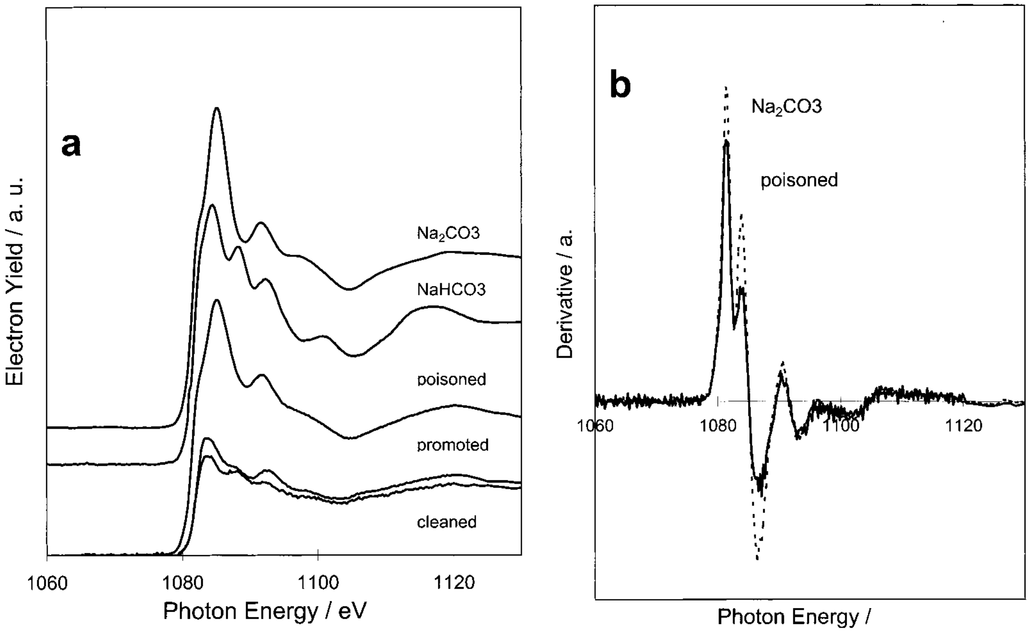

Figure 9. (a) Postreaction XANES spectra taken in electron yield mode after catalyst exposure to propene and oxygen at 588 K under promoted and poisoned conditions (see text for partial pressures). Also shown are reference spectra for the cleaned surface, Na_2CO_3 and $NaHCO_3$. (b) Derivative XANES spectra from poisoned surface and Na_2CO_3 reference sample.

$P_{propene}$ = 5.7) the clean surface rate is highest and the effect of EP least (r_{max}/r_0 = 1.1). As the propene content of the reactant gas increases ($P_{oxygen}/P_{propene}$ = 4.0), the clean surface rate decreases and effects of EP become more pronounced (r_{max}/r_0 = 2.2). Finally, under propene-rich conditions ($P_{oxygen}/P_{propene}$ = 2.0) the relative effect of EP is highest (r_{max}/r_0 = 2.3) and the overall activity is lowest. These results provide an important clue for interpretation of the kinetic data: the system is poisoned by excess propene and this effect is somehow diminished by the electrochemically supplied Na.

Figure 2 shows that, on the clean surface and at low propene partial pressure, the reaction is essentially first order in propene, tending to zero order behavior at high propene pressure. A rate maximum is observed when the surface concentration of the two reactants is optimal. In the promoted regime, Na enhances overall activity, the qualitative kinetic behavior is unchanged, *but the rate maximum shifts to higher propene partial pressure.* The poisoned surface exhibits low activity under all conditions. The corresponding kinetic behavior as a function of oxygen partial pressure (Figure 3) shows a similar transition from first order to zero order kinetic with increasing P_{oxygen}, although no rate maximum is accessible under our conditions, even at very high oxygen partial pressure. Thus we have a Langmuir–Hinshelwood reaction which is subject to self-poisoning by propene: the kinetic behavior of our thin film catalyst is in good accord with that found for propene oxidation over Pt/Al_2O_3 catalysts.[10] We propose that the Na promoter works electronically by weakening and strengthening, respectively, the Pt–propene and Pt–oxygen adsorption bond strengths, thus increasing the oxygen coverage and hence the rate. This argument is based on the idea that Na is an electropositive promoter which should therefore enhance (inhibit) the adsorption of electronegative (electropositive) adsorbates such as oxygen (propene) by transfer of electron density to (from) the coadsorbate. We have discussed this in detail elsewhere.[7] Direct evidence in support of these ideas is provided by experiments on single-crystal surfaces of Pt.[11,12] The effect of EP should therefore be most pronounced under propene-rich conditions, as indeed is found (Figure 1). A similar explanation was advanced for the (much more effective) promotion of the NO + propene reaction by electrochemically supplied Na.[7] What causes poisoning? As will be demonstrated, poisoning is due to excessive buildup of Na compounds at high Na loadings (very negative catalyst potential) resulting in blocking of the active surface. The identity of these Na compounds will be discussed below.

The shift of the rate maximum to higher propene partial pressure on the Na promoted surface relative to the clean surface is interesting (Figure 2). This may be understood as follows. As argued above, Na decreases the adsorption strength of propene and increases that of oxygen. Therefore, for a given oxygen partial pressure, the presence of Na should require a *higher* partial pressure of propene in order to optimize the coverage of this reactant, as observed. Similarly, we may understand the dependence of the strength EP effect on gas phase composition (Figure 1). When the gas phase is oxygen rich, the rate is zero order with respect to oxygen and so there is little or no promotion due to Na. With increasing propene partial pressure, the effects of EP become apparent as the hydrocarbon starts to compete more effectively for adsorption sites. These observations are in good agreement with previous findings for EP of CO oxidation and ethylene combustion over Pt/Na–β''-alumina[4,5,13] as a function of oxygen/fuel ratio.

The XPS and XANES data provide valuable information about the nature of the surface species present under promoted and poisoned conditions. First, it is useful to recall that we have previously demonstrated by XPS[7] (i) that electrochemical promotion of the NO + propene reaction is due to reversible spillover of electrochemically generated Na species from solid electrolyte to the Pt catalyst surface, (ii) that this electrochemically supplied Na is equivalent to vacuum-evaporated sodium, and (iii) that under those reaction conditions the sodium forms $NaNO_2$ and $NaNO_3$, which, depending on the loading, can either promote or poison the reaction.

In the present case, the Na KLL Auger data (Figure 4) show that the poisoned surface is associated with substantially more Na-containing compound(s) than the promoted surface. These Na surface compounds are stable at 588 K (typical reaction temperature) but readily decomposed by pumping Na away from the catalyst film. The Na 1s XPS results (Figure 5) confirm the stability of the Na compound at reaction temperature and its destruction by electropumping of Na away from the surface. However, they are insensitive to the difference in Na loading between the promoted and poisoned conditions, in contrast to the Na KLL Auger spectra. This difference is understandable in terms of the different electron escape depths associated with the AE and XP spectra. The kinetic energy of the Na 1s photoelectrons is ~180 eV, corresponding to a sampling depth of ~8 Å for the analyzer-sample geometry employed in our measurements. On the other hand, the kinetic energy of the Na KLL Auger electrons is 990 eV, giving a sampling depth of around 25 Å.[14] Thus the two types of measurement probe different thicknesses. The implication is that, on the poisoned surface, much of the Na compound is present in the form of three-dimensional crystallites with dimensions ≥30 Å whose bulk Na content is effectively “invisible” in the Na 1s XP spectrum.

What are these surface compounds? Na 1s XP spectra are insensitive to the chemical state of Na,[15] and it is therefore unsurprising that no chemical shifts are detectable between the poisoned and promoted cases (Figure 5). (As explained above, the residual Na 1s emission visible in the clean surface spectrum can be assigned to Na in the underlying β''-alumina visible through cracks and imperfections in the Pt film.) However, the Na KLL Auger spectra for the poisoned and promoted cases do exhibit pronounced differences in line shape (Figure 4, spectra 1 and 2); changes also occur as a result of heating (Figure 4, spectrum 3). As for the Na 1s data, the residual emission from the clean surface is due to the Na–β''-alumina. Detailed analysis of these spectra in terms of Na electronic structure is not possible because there have been no systematic studies of the Na KLL line shape and emission energy. However, they do serve to distinguish different Na environments.[16] It thus appears that here are significant chemical differences between the promoted, poisoned, and heated states, a conclusion which is confirmed and clarified by the C 1s spectra discussed below.

The Pt 4f XP spectra (Figure 6) are revealing in regard to the extent of loading and morphology of the Na surface compounds. The relevant electron escape depth is ~15 Å, indicating that on the poisoned surface, where the Pt emission is almost completely quenched, the average thickness of the Na compound deposit is more than ~45 Å. Note that the Pt 4f photoemission on the promoted surface is also significantly attenuated (~50%; equivalent to a uniform layer of ~10 Å). As noted above, the Na ion current transients observed during preparation of the promoted and poisoned surfaces in the XANES experiments also permit estimates of the Na coverage to be made. For the promoted catalyst the result is ~13 monolayers at V_{WR} = −100 mV. Clearly, since this catalyst is active, i.e., Pt sites are exposed to the reactants, the implication is that much of the Na promoter phase must be present as three-dimensional crystallites. The corresponding estimate for the poisoned catalyst is ∼100 monolayers of Na compound. Thus the two types of measurements differ by a significant factor in regard to the absolute amounts of Na compound present on both the promoted and poisoned surfaces. However, given that the Cambridge and Daresbury measurements were carried out on different samples and not under identical conditions, the level of agreement is satisfactory (the amount of Na at the surface is a function of temperature, reactant partial pressures, and the exact value of V_{WR}). More importantly, these results lead us to a significant conclusion. Since the promoted surface is catalytically active, the above values for the corresponding thickness of a *uniform* film of Na compound imply that in the promoted case some of the surface exposes promoter-modified Pt sites while the rest is covered by three-dimensional crystallites of the Na compound.

The C 1s XP spectra provide information as to the chemical identity and stability of the Na compound(s) present on the Pt surface under promoted and poisoned conditions. Figure 7 shows spectra taken from the poisoned surface and after heating this surface to 588 K (spectra 1 and 2, respectively). It is clear that heating has little effect. The feature at 289.3 eV may be unambiguously assigned to carbonate;[17] that at 284.6 eV is assigned more tentatively to a species containing C−O−C bonds.[18] On the promoted surface (spectrum 3) the overall C 1s intensity is weaker than on the poisoned surface, as expected, and three peaks are visible. The weak emission at *289.3 eV* is asssigned to carbonate and/or bicarbonate;[18] the peak at 287.4 eV is consistent with a stable Na−CO complex[19] of the type readily fomed on alkalized transition metal surfaces, and that at 283.5 eV could be due to hydrocarbonaceous species,[20] though this assignment is less certain. Heating the promoted surface to 588 K resulted in spectrum 4. Here, in contrast with the poisoned case, chemical changes appear to have occurred. The Na−CO complex has been decomposed, the hydrocarbonaceous species have attenuated, and the emission in the carbonate/bicarbonate region is enhanced. Thus it appears that at the reaction temperatures used here (∼600 K) the Na−CO would not be present, the main carbon-containing Na compounds being sodium carbonate and/or bicarbonate. Pumping Na away from this surface (spectrum 5; +500 mV) results in residual emission (282.6 eV) assigned to carbidic carbon.[20] At the same time, the pressure rose in the vacuum chamber, indicating electrochemical decomposition of the Na compounds with desorption of carbon-containing molecules. It is possible that the hydrocarbonaceous species detected on the promoted surface at 283.5 eV BE correspond to reaction intermediates formed during propene oxidation. Although the evidence on this point is not conclusive, similar species have been detected on the "frozen" promoted Pt surface following the propene + NO reaction.[7]

The above assignments are supported by the oxygen 1s spectra (Figure 8). Spectrum 1 is from the electrochemically cleaned surface. There are two components: one from the β''-alumina and the other due to the Pt, distinguishable by their different dependencies on V_{WR}. The poisoned surface (spectrum 4) shows a single unambiguous sodium carbonate feature.[18,20] The promoted surface looks quite different (spectrum 2) with oxidic emission[18,20] at 530.3 eV and a weaker feature at 534.3 eV. The latter falls within the rage of O 1s BEs reported for alkali metal−CO complexes on transition metal surfaces and therefore tends to confirm the conclusion drawn from the C 1s spectrum of the promoted surface. Heating the promoted surface to 588 K removes the 534.3 eV emission, strongly supporting the conclusion drawn from the C 1s spectra, namely that a Na−CO complex is destroyed. At the same time the oxidic emission is replaced by a peak at 531.1 eV, close to the "thick layer" Na_2CO_3 peak at 531.8 eV (spectrum 4). Thus the carbon and oxygen XP spectra show that (i) poisoning is due to a relatively thick deposit of sodium carbonate, (ii) the Na−CO complex does not survive at reaction temperature and is probably an artifact of the method used for "freezing" and transferring the sample from the reactor cell to the UHV analysis chamber, and (iii) that the promoter phase also contains mainly sodium carbonate; the similar emission intensities in the two cases confirm that on the poisoned surface much of the carbonate must be present as three-dimensional crystallites.

The formation of three-dimensional crystalline sodium carbonate on the surface of the poisoned catalyst is strongly confirmed by the XAFS results shown in Figure 9; in particular, the derivative spectra show excellent agreement with the Na_2CO_3 reference sample. In the promoted regime the data are limited by instrumental resolution and signal-to-noise ratio, and of course the two-dimensional Na−CO complex proposed on the basis of the C 1s and O 1s XPS data cannot be detected by this technique.

Conclusions

Pt-catalyzed propene combustion is subject to electrochemical promotion by Na, the response of the system depending strongly on reactant gas composition. The effect is greatest under fuel-rich conditions where the reaction exhibits zero (or negative) order in propene and positive order in oxygen.

Up to moderate sodium loadings, EP occurs due to electropumped Na enhancing the chemisorption of oxygen while inhibiting the adsorption of propene. At sufficiently negative catalyst potentials, the metal surface is deactivated by excessive accumulation of a sodium compound. The promotion and poisoning behavior is fully reversible as a function of catalyst potential.

Na 1s, Pt 4f, and C 1s XP spectra and the Na K edge XANES show that the poisoned surface carries a substantially greater loading of Na compound than does the promoted surface. The Na KLL Auger and O 1s XP spectra, supported by current transient data, indicate that a substantial fraction of the Na compound on the promoted surface must be present as three-dimensional crystallites.

C 1s and O 1s XPS and XAS data clearly show that the three-dimensional compound responsible for poisoning is sodium carbonate.

The promoter phase consists also consists of sodium carbonate. The Na−CO surface complex detected in the C 1s and O 1s XP spectra is probably an experimental artifact.

The promoter and poison phases are stable at reaction temperature; however, they are rapidly destroyed by electropumping Na away from the surface. This confirms their direct participation in the electrochemically modified catalytic reaction.

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References and Notes

(1) Vayenas, C. G.; Bebelis, S.; Yentekakis, I. V.; Lintz, H.-G. *Catal. Today* **1992**, *11*, 303.

(2) Vayenas, C. G.; Bebelis, S.; Despotopoulou, M. *J. Catal.*. **1991**, *128*, 415.

(3) Harkness, I. R.; Hardacre, C.; Lambert, R. M.; Yentekakis, I. V.; Vayenas, C. G. *J. Catal.* **1996**, *160*, 19.

(4) Bebelis, S.; Vayenas, C.G. *J. Catal.* **1989**, *118*, 125.

(5) Harkness, I. R.; Lambert, R. M.; *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1425.

(6) Kaloyannis, A. C.; Pliangos, C. A.; Yentekakis, I. V.; Vayenas, C. G. *Ionics* **1995**, *1*, 159.

(7) Yentekakis, I. V.; Palermo, A.; Filkin, N. C.; Tikhov, M. S.; Lambert, R. M. *J. Phys. Chem. B* **1997**, *101*, 3759.

(8) Yentekakis, I. V.; Lambert, R. M.; Tikhov, M. S.; Konsolakis, M.; Kiousis V. *J. Catal.* **1998**, *176*, 82.

(9) Williams, F.; Aldao, C. M.; Palermo, A.; Lambert, R. M. *Surf. Sci.* **1998**, in press.

(10) Yu Yao, Y.-F. *J. Catal.* **1984**, *87*, 152.

(11) Pirug, G.; Bonzel, H. P.; Broden, G. *Surf. Sci.* **1982**, *122*, 1.

(12) Windham, R. G.; Bartram, M. E.; Koel, B. E. *J. Phys. Chem.* **1988**, *92*, 865.

(13) Yentekakis, I. V.; Moggridge, G.; Vayenas, C. G.; Lambert, R. M. *J. Catal.* **1994**, *146*, 292.

(14) Watts, J. F. *Vacuum* **1994**, *45,* 653.

(15) Wagner, C. D.; Riggs, W. M.; Davies, L. E.; Moulder, J. F. In *Handbook of X-ray Photoelectron Spectroscopy;* Muilenberg, G. E., Ed.; Perkin-Elmer, Eden Prairie, MN, 1978.

(16) Palermo, A.; Holgado Vazquez, J. P.; ALee, A. F.; Tikhov, M. S.; Lambert, R. M. *J. Catal.* **1998**, *177*, 259.

(17) Seyller, T.; Borgmand, D.; Wedler, G. *Surf. Sci.* **1998**, *400*, 63.

(18) Paal, Z.; Schlögl, R.; Ertl, G. *J. Chem. Soc., Faraday Trans.* **1992**, *88,* 1179.

(19) Kiskinova, M.; Pirug, G.; Bonzel, H. P., *Surf. Sci.* **1983**, *133*, 321.

(20) Wagner, C. D.; Zatko, D. A.; Raymond, R. H. *Anal. Chem.* **1980**, *52* (2), 1445.