Kinetic study on the selective catalytic oxidation of 2-propanol to acetone over nickel foils

Ali H. Ali, Francisco Zaera*

Department of Chemistry, University of California, Riverside, CA 92521, USA

Abstract

The kinetics of the catalytic oxidation of 2-propanol with molecular oxygen on clean and oxygen-pretreated Ni foil samples was studied by using a microbatch reactor with mass spectrometry detection. It was found that, under the right conditions, high selectivity for acetone formation can be achieved in this system. Specifically, it was determined that high partial oxidation selectivity requires the use of temperatures below 700 K and oxygen partial pressures higher than stoichiometric, i.e. oxygen-to-alcohol ratios above 1:2. Zero- and half-order kinetics with respect to 2-propanol and oxygen pressures, respectively, were observed for the conversion of 2-propanol to acetone on the clean Ni catalyst. A thin oxide-like layer was determined to be the active catalyst for this reaction, and the rate of oxidation was found to be significantly higher on oxygen-pretreated Ni surfaces. Our kinetic evidence also indicates that the undesirable complete oxidation of the alcohol to CO_2 and water is mainly a sequential reaction that takes place on the acetone produced from the alcohol, not a primary alcohol oxidation step. Finally, it was found that dehydrogenation of 2-propanol to acetone in the absence of oxygen is also possible, but occurs at a significantly slower rate than when oxygen is present in the gas mixture, and leads to poisoning of the surface of the catalyst via the deposition of carbonaceous deposits. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic oxidation; 2-propanol; Acetone; Nickel catalysts; Dehydrogenation; Oxidation kinetics

1. Introduction

The direct selective oxidation of alcohols could in principle be used for the manufacturing of a variety of useful oxygenates [1–3]. Unfortunately, the oxidation of alcohols to specific desirable carbonyl compounds is in general not selective enough for practical applications; only the selective oxidation of methanol to formaldehyde is industrially viable today [2]. On the one hand, the use of oxygen makes the endothermic dehydrogenation of alcohols to aldehydes and ketones

exothermic. On the other hand, however, total oxidation products such as CO_2 and H_2O are the ones favored thermodynamically. It is clear that some form of kinetic control is necessary to achieve selectivity in alcohol oxidation for the synthesis of aldehydes, ketones and other oxygen-containing hydrocarbons.

Traditionally, the oxidation of alcohols is done by using stoichiometric quantities of inorganic oxidants, mainly chromium salts [4,5]. Those oxidants are fairly expensive, and also generate large volumes of heavy-metal waste. More recently, a number of homogeneous oxidation catalysts have been developed for alcohol conversion [6,7], but unfortunately, those require the use of environmentally undesirable solvents, noticeably chlorinated hydrocarbons. An

* Corresponding author. Tel.: +1-909-787-5498;
fax: +1-909-787-3962.
E-mail address: francisco.zaera@ucr.edu (F. Zaera).

aerobic greener process involving a Pd(II) homogeneous catalyst looks somewhat promising, even though that system is not applicable for a wide range of alcohols, and requires high pressures [7]. The search for selective oxidation procedures continues, and the use of heterogeneous catalysts with oxygen (or air) as the oxidant is particularly promising in this endeavor.

Brief studies on the oxidation of alcohols over nickel-based catalysts have suggested that such a metal may be suitable for selected partial oxidation processes [8–14]. In early studies with Raney nickel in the 1960s, primary alcohols were used as hydrogen donors (via their conversion to aldehydes) for the selective reduction of alkenes, nitriles, nitro, and carbonyl compounds [8], and mild oxidants were also tried to selectively oxidize branched primary, secondary, and tertiary alcohols [9,10]. Unfortunately, this idea proved to be of limited use, because decarbonylation is sometimes observed with primary and tertiary alcohols [10]. Metallic nickel from nitrates supported on silica gel were also shown to oxidize primary, benzylic, allylic, and secondary alcohols to the corresponding aldehydes and ketones at low temperatures [12]; a mechanism that starts with the formation of a NO_2 radical has been suggested for that reaction. In terms of the use of nickel(II) oxides, Hoodless et al. found that the reaction rate order for the deep oxidation of propane to carbon dioxide and water with such catalysts exhibits increasing values with increasing temperature, an observation that the authors linked to an increase in the availability of reactive O^- species [13]. The same research group also reported that methanol suppresses alkane oxidation and leads to the reduction of the surface, and that under appropriate reaction conditions formaldehyde is the major product.

More recent studies by Christoskova et al. reported contradicting opinions on the status of the surface of the nickel catalyst during the room temperature oxidation of alcohols and other organic molecules in aqueous solutions, suggesting the formation of both a high oxide form, $(OH)_2NiO_x \cdot mH_2O$ (where the nickel atoms are in the 4+ oxidation states), and nickel peroxides [15]. Nickel oxide-hydroxide is also believed to be the active phase in the electrochemical selective oxidation of organic compounds under mild conditions, where primary and secondary alcohols are readily oxidized to aldehydes and ketones without interference

from other functional groups [16]. However, the proposals derived from all these early catalytic studies about the species that may form on the surface during hydrocarbon oxidation reactions on nickel-based catalysis are highly speculative, and await direct spectroscopic confirmation.

Surface-science research on the oxidation of alcohols on solid substrates have also been scarce. Based on studies on the decomposition of alcohols and other oxygenates on transition metals, it has been concluded that the first-step in alcohol thermal conversion reactions on either clean or oxygen-covered transition metal surfaces is the formation of a stable alkoxide intermediate [17–29]. That alkoxide can then undergo a number of dehydrogenation steps, the selectivity of which depends in part on the identity of the transition metal and, perhaps more importantly, on the presence of oxygen on the surface. Specifically, the promotion of non-selective decomposition of alcohols to CO, H_2, and hydrocarbons is common on clean surfaces of metals, such as Pt(1 1 1) [18], Pd(1 1 1) [19,28], Ni(1 1 1) [17] and (1 1 0) [24], and Rh(1 1 1) [30], but not on clean Cu(1 1 0), where very little reactivity is observed [31]. On the other hand, some selective dehydrogenation of primary and secondary alcohols to the corresponding aldehydes and ketones has been reported on a number of oxygen-covered metal surfaces [30,32,33]. The formation of these oxygenates is believed to occur via a rate-limiting β-hydride elimination step from the alkoxides, a reaction perhaps aided by the presence of either OH or O atoms adsorbed on the surface [30,34]. A few additional surface science studies have been performed on alcohol oxidation reactions on oxide surfaces. For instance, methanol was found to always dehydrogenate to methoxide and to then undergo selective oxidation to formaldehyde on clean $ZrO_2(1 1 0)$ [35] and $SnO_2(1 1 0)$ [36]. By contrast, dehydration to olefins is seen on some early transition metals [37] as well as on acidic catalysts such as $TiO_2(0 0 1)$ [38] and ZnO(0 0 0 1)–Zn [39]. One thing that has become clear from these studies is the fact that adsorbed oxygen plays a major rule in determining the product selectivity during alcohol decomposition.

Recent surface-science studies on the oxidation of alkyl groups on clean and oxygen-covered surfaces are also quite relevant to our catalytic work reported here. This is so because adsorbed alkyl moieties are proposed to form an alkoxide surface intermediate

similar to that produced when starting with alcohols as reactants. The selective oxidation of either ethyl or 2-propyl iodide, to acetaldehyde and ketone respectively, has been reported on oxygen-covered Rh(1 1 1) [40] and Ni(1 0 0) [34] surfaces. In the case of rhodium, it has been suggested that the C–I bond-scission step that leads to the formation of alkyl species is rate limiting, and that it is followed by an immediate oxygen addition to yield an alkoxide which then converts into the aldehyde or the ketone. An analogous mechanism appears to apply to the case of *t*-butoxide groups produced by activation of either *t*-butyl iodide or *t*-butanethiol on Rh(1 1 1)–*p*(2 × 1)–O surfaces [41].

We in our laboratory have carried out some surface-science studies on the mechanism of partial oxidation reactions on nickel substrates [34,42–45]. In particular, the selectivity in the conversion of either 2-propanol or 2-propyl iodide (the precursor used for the preparation of surface 2-propyl intermediates [42,43,46]) with oxygen on Ni(1 0 0) was found to depend on the coverage of oxygen on the surface. A particularly promising observation from that work is the fact that, even in the case of 2-propyl, some acetone is produced on nickel surfaces, if only when partially covered with oxygen [34,44,45]. It was determined that the conversion of the 2-propyl groups involves the low-temperature formation of a 2-propoxide species, an intermediate that can also be prepared by the facile dehydrogenation of adsorbed 2-propanol. 2-Propoxide then yields acetone via a rate-limiting β-hydride elimination step [34]. The presence of hydroxide groups on the surface appears to facilitate this process [44].

In general terms, both catalytic and surface science data from past studies suggest that, under the right conditions, nickel surfaces may be capable of selectively catalyzing partial oxidation reactions [44,45]. A number of criteria has been identified for the feasibility of such processes: (1) the need of nickel surface atoms in order to promote the activation of the initial reactants, either the alcohol or the alkane (the nature of these nickel atoms—oxidation state, immediate surrounding environment—is still to be determined); (2) the need of oxygen atoms in the proximity of the alkyl groups during alkane oxidation in order to facilitate the insertion step that leads to alkoxide formation (this oxygen could be located in the immediate sub-surface

region); and (3) the desirability of having surface hydroxide groups on the surface to enhance the partial oxidation pathway. It has also been concluded that: (1) the formation of ketones seems to be easier than the production of aldehydes; and (2) alkenes appear to not be direct intermediates in the conversion of alkyl groups to aldehydes and ketones. This latter conclusion is particularly interesting, because alkenes can in fact be oxidized catalytically [47]. Perhaps alkenes hydrogenate to alkyl groups on the surface before undergoing oxygen incorporation.

In this report, a kinetic study is presented on the catalytic oxidation of 2-propanol with oxygen on Ni foils. Both rates and selectivities for this conversion were characterized as a function of alcohol and oxygen partial pressures, temperature, and nature of the surface, in order to search for the conditions needed for maximum selectivity toward oxidation to acetone. 2-Propanol conversion to acetone is not of industrial interest in itself, but was chosen here as a prototype for the more generic family of alcohol oxidation reactions. It was found that high yields for acetone production requires both low temperatures, below 700 K, and high oxygen-to-2-propanol partial pressure ratios. The reaction rate law for alcohol formation was estimated to be approximately half-order in oxygen and zero-order in the alcohol. The formation of CO_2 and water was found to occur mainly via the sequential oxidation of the acetone produced by the initial step. It was also determined that the active catalyst is the oxide-like thin film that forms soon after exposures of the surface to the reaction mixture, and that the reaction rate is higher on oxygen-pretreated Ni surfaces. A detailed mechanism is proposed here to account for these observations.

2. Experimental

The experiments reported here were carried out by using a recirculating batch reactor described in detail elsewhere [48]. Briefly, the reactor, a stainless steel loop with a total volume of $200 \, cm^3$, is evacuated with a mechanical pump to a base pressure of about $3 \times 10^{-2} \, Torr$, filled with the reacting gases (2-propanol and oxygen, in that order), and topped off with argon to a final pressure of 500 Torr. The gases are mixed with a recirculation bellows pump until

complete mixing is achieved, and the nickel sample is then heated to the reaction temperature. The time evolution of the partial pressures of the reactants and products is followed continuously by using a mass quadrupole spectrometer located in a separate chamber and connected to the reactor via a capillary tube. The collection and storage of data is accomplished by using a personal computer interfaced to the mass spectrometer. Absolute pressures in the reactor are measured by using a capacitance manometer (Baratron gauge) directly attached to the reactor loop.

The catalyst, a square 10 mm × 10 mm nickel foil, 0.5 mm thick (Aldrich, +99.98% purity), was spot-welded directly to two 20 mm long, 2 mm thick nickel wires (Aldrich, +99.995% purity) attached to copper feedthroughs. This sample was heated resistively by using a variable autotransformer, and its temperature continuously monitored by using a chromel–alumel thermocouple spot-welded to the foil. Heating of the sample was checked by visual inspection through a viewport placed in front of the sample compartment, and deemed homogeneous throughout the whole foil. Cleaning of the catalyst was carried out before each kinetic run by successive 1 min exposures to oxygen and hydrogen at 1000 K followed by annealing at 1000 K under vacuum. It was determined that an oxide layer starts to form on the surface in the oxygen atmosphere above 775 K (a dull coating develops on the surface), but that such film is reduced back to the metallic state under the hydrogen atmosphere above 600 K (the sample regains its shinny appearance).

Anhydrous 2-propanol and acetone were purchased from Aldrich (99.5 and 99.9% purity, respectively), and freeze-pumped several times before use. These compounds were kept in glass ampoules, and their vapors were introduced in the reactor via a gas manifold directly attached to the main reactor loop. Oxygen (99.99% purity) and argon (99.999% purity) were purchased from Matheson, and hydrogen (99.999% purity) was acquired from Liquid Carbonic. All the gases were used as supplied, but their purity was checked periodically by mass spectrometry.

The 45 and 43 amu ions were chosen to follow the partial pressures of 2-propanol and acetone, respectively, during the kinetic experiments, but the identity of those compounds was corroborated by simultaneously recording and comparing the signals for other

(15, 27, 41, 58) mass-to-charge ratios. The 2, 18, 28, 32, and 44 amu peaks in the mass spectra were employed to follow the time evolution of the partial pressures of hydrogen, water, carbon monoxide, oxygen, and carbon dioxide, respectively. The mass spectrometer signal intensities of the reacting gases were calibrated against readings from the Baratron pressure gauge in the reactor in order to convert them directly to partial pressures, and turnover number (TON) and turnover frequencies (TOF), reported in molecules per Ni surface atom and TON per second, respectively, were estimated by assuming an atomic surface density of $\sim 1.75 \times 10^{15}$ metal atoms/cm^2 (an average of those for the (1 0 0) and (1 1 1) faces).

3. Results

3.1. General considerations

The catalytic conversion of 2-propanol on nickel surfaces in the presence of gas-phase oxygen was studied by performing a number of systematic isothermal kinetic experiments as a function of temperature and partial pressures of the reactants. Fig. 1 displays the raw data obtained from a typical run, in this case for a mixture of 30 Torr of 2-propanol and 15 Torr of oxygen and a reaction temperature of 705 ± 2 K: shown is the time evolution of the partial pressures of hydrogen (2 amu), water (18 amu), carbon monoxide (28 amu), oxygen (32 amu), acetone (43 amu), carbon dioxide (44 amu), and 2-propanol (45 amu). The mass spectrometer signal intensities of the relevant gases were normalized to that of Ar (used to reach a total pressure of 500 Torr) in order to correct for potential fluctuations due to gas heating or pressure differentials in the reactor. A number of additional possible products, including propene, propane and methane, were searched for but not detected. The contribution of the alcohol to the signal for the 43 amu mass spectrometer peak was subtracted in all measurements by using that of the 45 amu trace, appropriately scaled based on the cracking pattern of the alcohol, in order to estimate the partial pressure of the acetone produced.

A number of observations derive from the data presented in Fig. 1. For one, it is apparent that the main product from the reaction of 2-propanol with O_2 is
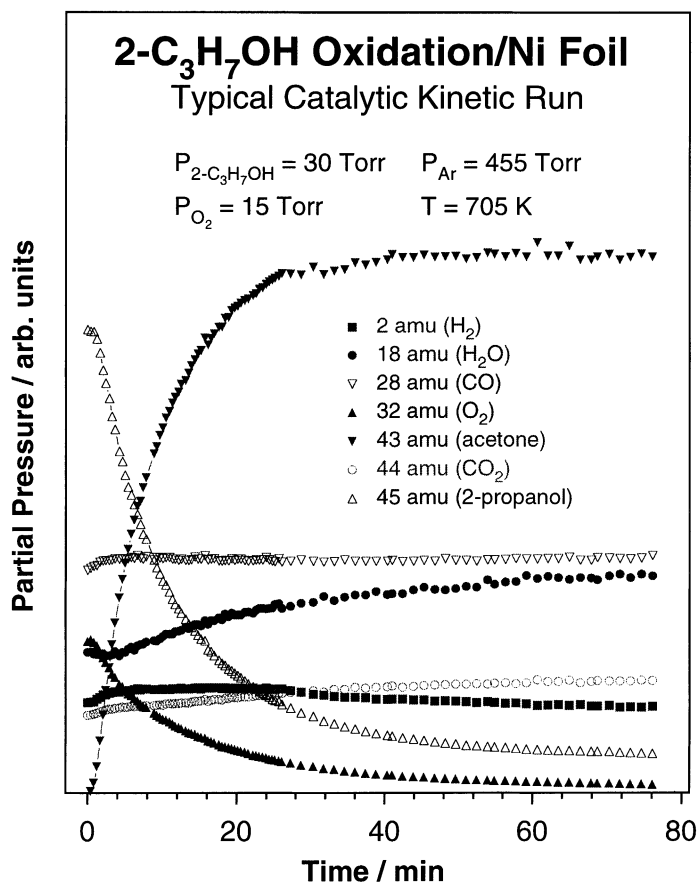
Fig. 1. Typical isothermal kinetic run for the oxidation of 2-propanol with oxygen over a nickel foil at 705 ± 2 K. The partial pressures used in this example were 30 and 15 Torr for 2-propanol and oxygen, respectively, and the total pressure was taken to 500 Torr with argon. Shown in this figure is the temporal evolution of the partial pressures of the relevant reactants and products, namely, H_2 (2 amu), H_2O (18 amu), CO (28 amu), O_2 (32 amu), acetone (43 amu), CO_2 (44 amu), and 2-propanol (45 amu). The major product detected in all cases was acetone, but some H_2O, H_2, CO, and CO_2 are also produced.

acetone, although detectable amounts of water, hydrogen, carbon monoxide, and carbon dioxide are formed as well. Moreover, based on the fact that both the alcohol and the oxygen are consumed almost completely after about 50 min of the reaction, it can be established that the oxidation of 2-propanol to acetone is approximately stoichiometric, i.e. it follows the equation:

$$CH_3CH(OH)CH_3(g) + \tfrac{1}{2}O_2(g)$$
$$\rightarrow CH_3COCH_3(g) + H_2O(g),$$
$$\Delta H = -44.1 \, \text{kcal/mol} \qquad (1)$$
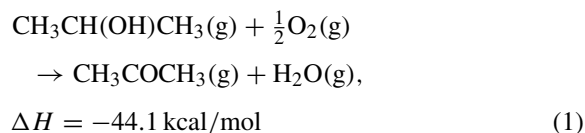
Notice, however, that the conversion of the alcohol is also accompanied by the production of small amounts of CO_2 and water. In fact, after calibration, it was determined that the production of acetone in the case illustrated in Fig. 1 amounts to only about 76% of the original propanol. It should also be said that the initial high levels of CO, CO_2, H_2 and H_2O are due to background gases in the mass spectrometer chamber, and do not contribute to the reaction. Only the changes in partial pressures with reaction times are relevant to the kinetic experiments. These and other aspects of the alcohol oxidation processes are explored in more detail below.
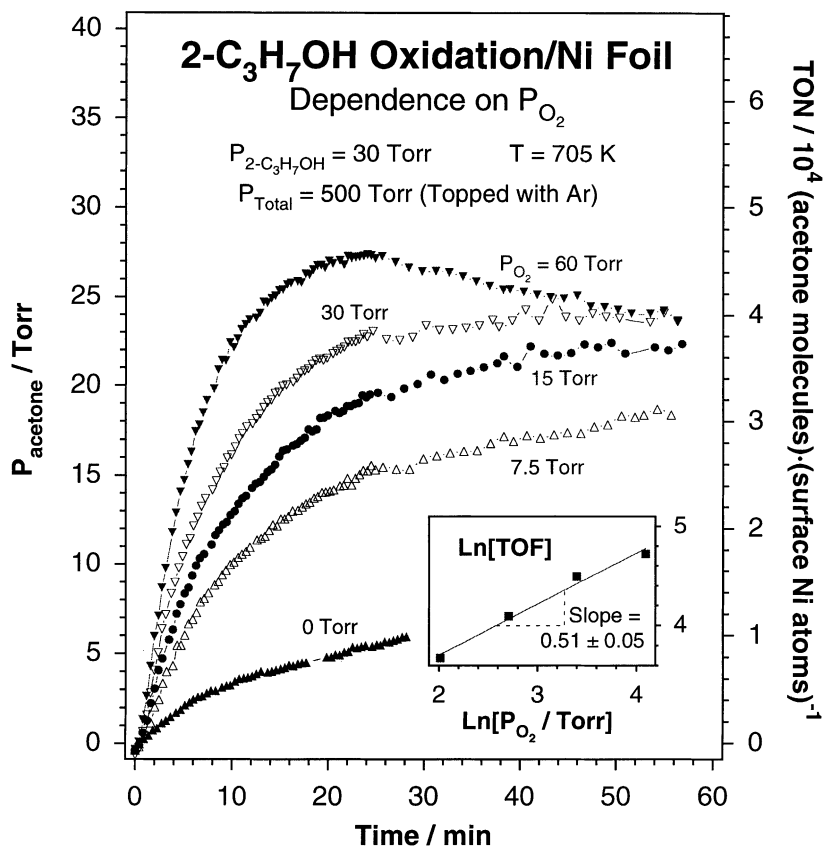
Fig. 2. Dependence of the kinetics of oxidation of 2 propanol on the partial pressure of oxygen over a Ni foil at 705 ± 2 K. The initial pressure of oxygen in the reaction mixture was varied from 0 to 60 Torr, while that of 2-propanol was kept at 30 Torr. This figure shows the temporal evolution of the partial pressure of acetone (43 amu), in both Torr and turnover number (TON = molecules/Ni surface atom s) units. The inset shows a Ln–Ln plot of the initial rate of formation of acetone (in turnover frequency, TOF = TON/time in seconds) vs. oxygen pressure, as calculated from the raw kinetic data. The order of the reaction with respect to oxygen was estimated directly from the slope of that graph to be 0.51 ± 0.05. Also, significant dehydrogenation without the intervention of oxygen takes place in the $P_{O_2} = 0$ and 7.5 Torr cases. The maximum yield of acetone and the initial rates for each of these runs are given in Table 1.

3.2. Pressure dependence

Fig. 2 shows the effect that changing the partial pressure of oxygen (from 0 to 60 Torr) has on the oxidation of 2-propanol. The same 30 Torr initial pressure of the alcohol was used in all these runs, and the temperature was always kept constant at 705 ± 2 K. It can be seen here that the maximum amount of acetone produced in these experiments increase with increasing oxygen partial pressure. In particular, a maximum in acetone production of 27 Torr (i.e. about 91% of the initial amount of alcohol in the mixture) was reached

after about 20 min of reaction for the case of $P_{O_2} = 60$ Torr. Notice that the pressure of acetone falls after reaching the maxima in yield, in the oxygen-rich mixtures in particular, presumably because of its subsequent combustion to CO_2 and water (see below).

A gradual increase in reaction rate is also seen with increasing amounts of oxygen in the mixture, as manifested by the higher slopes of the pressure versus time curves. Initial rates were estimated by fitting empirical cubic polynomial functions to the raw kinetic data in this figure for the first 8 min of reaction and by taking the derivative of that function at time zero.

Table 1

Maximum acetone yields (Y_{max}) and initial acetone formation rates (R_{init}) as a function of P_{O_2} for the oxidation of 2-propanol with oxygen over clean and oxygen-pretreated Ni foils. $T = 705 \pm 2\,K$ and $P_{ROH} = 30\,Torr$ in all cases

Clean Ni foil			O$_2$-pretreated Ni foil		
P_{O_2} (Torr)	Y_{max}, % (t, min)	R_{init} (TOF)[a]	P_{O_2} (Torr)	Y_{max}, % (t, min)	R_{init} (TOF)[a]
0	[b]	16			
7.5	[b]	40	5	[b]	73
15	76 (60)	58	15	84 (27)	123
30	79 (45)	91	30	85 (23)	143
60	91 (22)	111	45	84 (20)	159
$\langle k_{exp} \rangle = 15 \pm 1\,TOF/Torr^{1/2}$			$\langle k_{exp} \rangle = 42 \pm 2\,TOF/Torr^{0.36}$		

[a] Error margin: ±15%.

[b] The maximum yields of acetone at P_{O_2} less than 15 Torr are not reported because of the early stopping of those reactions due to the large accumulation of carbon deposits on the surface.

The resulting rates are summarized in Table 1, and are also shown in a Ln–Ln plot in the inset of Fig. 2. The order of the reaction with respect to the oxygen partial pressure was determined from these data to be ∼0.51 ± 0.05, and the pseudo rate constant $\langle k_{exp} \rangle$ (the ratio of the initial rates to the square root of the oxygen pressure) was estimated to be about $15 \pm 1\,TOF/P_{O_2}^{1/2}$ (molecules/Ni atom s Torr$^{1/2}$).

The data in Fig. 2 also indicate that dehydrogenation of 2-propanol to acetone can occur in absence of oxygen ($P_{O_2} = 0\,Torr$), although in that case the reaction is accompanied by the production of hydrogen instead of water. Moreover, the reaction rate decreases significantly after less than 10 min of reaction, and the formation of black carbon deposits on the nickel foil is seen by the naked eye soon afterwards. Since no carbon deposition was observed when acetone was heated at the same temperature in the absence of oxygen, it is assumed that it is the alcohol the one that dehydrogenates to surface carbon. This direct alcohol dehydrogenation is also operative to some extent in the presence of oxygen, at least for the alcohol-rich mixtures, a fact indicated by the higher-than-stoichiometric acetone yields observed in those cases: in the case of $P_{O_2} = 7.5\,Torr$, for instance, the total yield of acetone reaches a value above 18 Torr, higher than the 15 Torr expected from the stoichiometry of Eq. (1). Also, extensive total oxidation occurs in those cases: 8 out of the 26 Torr of the alcohol consumed in the latter example must have undergone total oxidation. Relatively more hydrogen is formed under alcohol-rich conditions (compared to those with higher partial pressures of oxygen), and complete decomposition becomes apparent by the build-up of small amounts of carbon on the surface of the catalyst in the late stages of the reaction.

The dependence of the time evolution of the production of acetone as a function of 2-propanol initial pressure is shown in Fig. 3. In this case, a constant 15 Torr of oxygen was used, while the pressure of the alcohol was varied from 5 to 30 Torr, and the temperature was again kept constant at $705 \pm 2\,K$. Since the pressure of oxygen used in this series of experiments was always equal to or higher than the pressure needed for a stoichiometric mixture, the amount of acetone produced was found to be directly related to the amount of the alcohol used (the limiting reactant). Also, no direct dehydrogenation of alcohol to acetone and hydrogen was observed in these cases. Initial rates were calculated from these runs in the same way as before, and the order of reaction with respect to the alcohol was estimated by the slope of the Ln–Ln plot of those data (shown in the inset of Fig. 3) to be close to zero (more accurately, 0.11 ± 0.03). This indicates that the rate of acetone production is approximately independent of the pressure of alcohol, at least under the conditions used in these studies.

3.3. Temperature dependence

The effect of temperature on the reaction of 2-propanol with oxygen was studied by using mixtures of 30 Torr 2-propanol and 15 Torr oxygen. Fig. 4 shows the raw data acquired for the time dependence
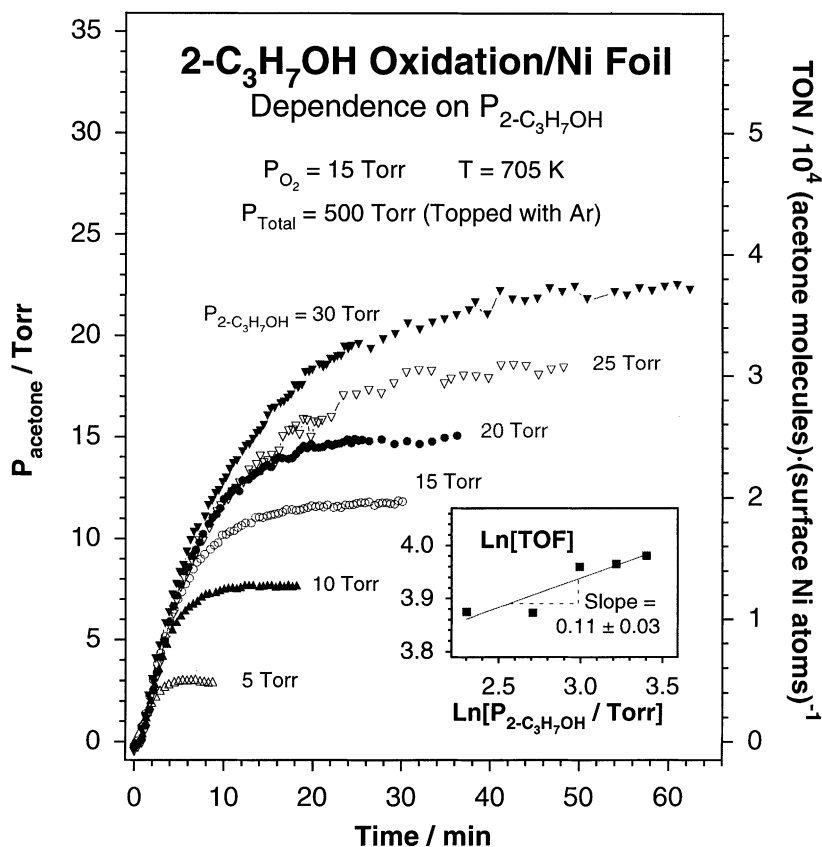
Fig. 3. Dependence of the kinetics of oxidation of 2-propanol on the partial pressure of 2-propanol over a Ni foil at 705 ± 2 K. An initial pressure of oxygen of 15 Torr was used in all cases, while that of 2-propanol was varied from 5 to 30 Torr. The figure shows the temporal evolution of the partial pressure of acetone (43 amu), in both Torr and turnover number units. The inset shows the resulting Ln–Ln plot for the acetone initial rate of formation vs. alcohol pressure, from which the order of reaction with respect to the alcohol was estimated to be 0.11 ± 0.03.

of acetone formation in the 663–757 K range. Some experimental problems limited these studies. For one, below 660 K the reaction is too slow to be studied reliably with our system, and above 760 K fast decomposition of the alcohol and/or the acetone also interferes with the reliability of the measurements. Even in the middle temperature range chosen here, induction periods were sometimes seen at the beginning of the kinetic runs because of delays in the reaction mixture reaching the mass spectrometer. Because of this, some fluctuations are also seen in some cases in the early stages of the reactions. In spite of these difficulties, however, it is clear that the initial rates for acetone formation (as well as those for alcohol

and oxygen consumption) increase with temperature, a normal Arrhenius-type behavior. Given that the reaction rate was found to be approximately half-order in oxygen and zero-order in the alcohol, the rate constant k for the reaction at each temperature was obtained from the slope of plots of the square root of the acetone pressure versus time estimated between 2 and 6 min times of the reaction. The fact that the $P^{1/2}$ versus time graphs in this time range turned out to be quite linear also corroborated the fact that the total order of reaction is ~ 0.5. The Arrhenius plot of $Ln(k)$ versus $1/T$ shown in the inset of Fig. 4 yielded an apparent activation energy for the formation of acetone of about 9 ± 1 kcal/mol. When direct $Ln(R_{init})$ versus
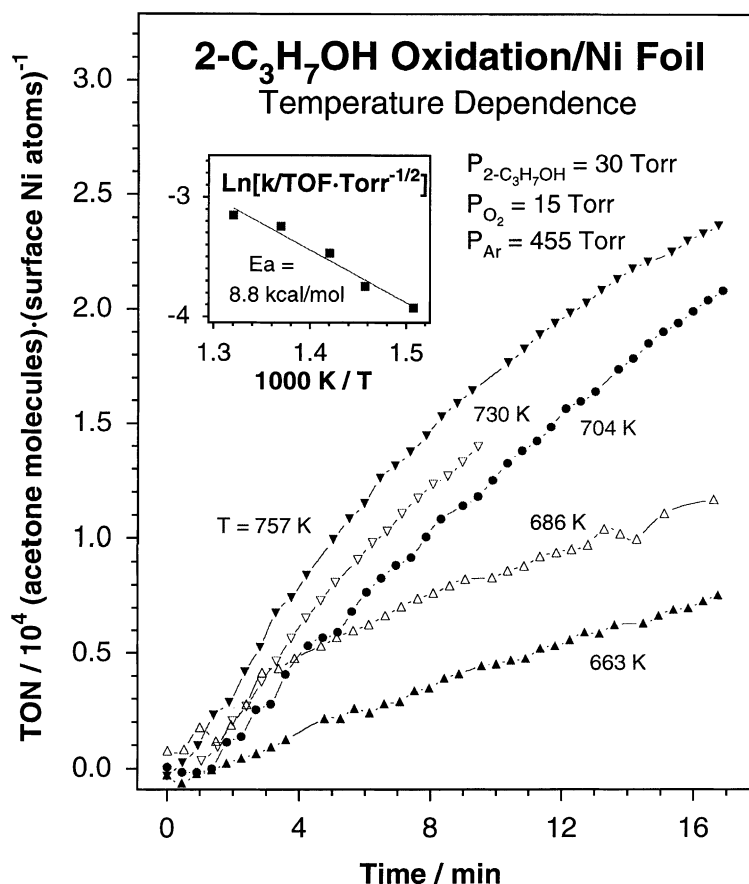
Fig. 4. Dependence of the kinetics of oxidation of 2-propanol with oxygen over a Ni foil on temperature. The reaction temperature was varied from 663 to 757 K. The main figure displays the temporal evolution of the acetone partial pressure for five different isothermal kinetic runs, while the inset shows an Arrhenius plot for the temperature dependence of the rate constant for acetone formation, in the form of $Ln(k)$ vs. $1/T$. The k values were obtained from plots of the square root of acetone pressure vs. time during the first 6 min of the reaction. The apparent activation energy of the reaction was estimated from the inset to be 9 ± 1 kcal/mol.

$1/T$ plots were used instead, an apparent activation of 14 ± 3 kcal/mol was obtained instead (not shown). This difference points to the relatively large margin of error associated with the temperature-dependence measurements, and cautions against using the value of the activation energy as the sole criteria to determine the reaction mechanism (see Section 4).

It was found that the reaction temperature also affects the selectivity of the reaction. The maximum conversion of the 2-propanol to acetone with a 30 Torr alcohol + 15 Torr O_2 mixture, 76%, was obtained at temperatures between 660 and 700; the conversion drops below 65% at higher temperatures, at which

point more CO_2 is produced. This will be discussed in more detail in the next section.

3.4. CO_2 production and other competing reactions

As discussed earlier, the selectivity for the oxidation of 2-propanol to acetone on nickel under the conditions reported here is high, but never 100%. The second major product in this reaction was identified to be CO_2. Our studies on the temporal evolution of CO_2 as a function of both alcohol and oxygen pressures and temperature, and the effect of those parameters on the selectivity for acetone production, are described next.
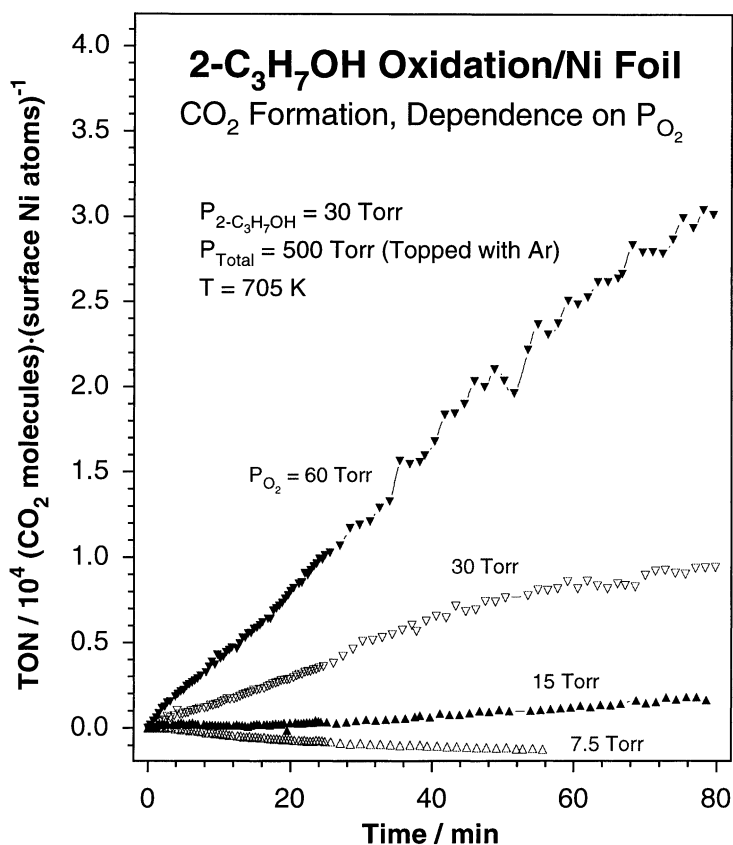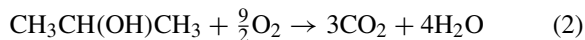
Fig. 5. Temporal evolution of the partial pressure of carbon dioxide (44 amu), in units of TON, as a function of initial partial pressure of oxygen for the kinetic runs shown in Fig. 2 ($P_{2\text{-propanol}} = 30$ Torr, $P_{O_2} = 0$–60 Torr, $T = 705 \pm 2$ K). The rate of carbon dioxide production shows a strong positive dependence on P_{O_2}.

Fig. 5 shows the effect of varying oxygen partial pressures on the time evolution of CO_2 production for the same runs as in Fig. 2. It can be clearly observed from this figure that both the rate of CO_2 formation and the total yield of CO_2 at a given time increase significantly with increasing oxygen partial pressure. Also, it is seen that the rate of CO_2 formation is slow at first but accelerates after 20–30 min. of reaction, after the maximum in acetone production has been reached. Indeed, the formation of CO_2 explains the fall in the pressure of acetone detected after the maximum in yield reached in the oxygen-rich mixtures (Fig. 2). In terms of the stoichiometry of the reactions involved in acetone and CO_2 formation, it is interesting to note that, for the mixture of 30 Torr of 2-propanol and 60 Torr oxygen (for instance), it was experimentally measured that

when about 27 Torr of the alcohol is consumed (at the point of maximum conversion, which is reached after about 20 min of reaction), ∼27 and 6 Torr of acetone and CO_2 are produced, respectively. Based on carbon mass balance arguments, the 6 Torr of CO_2 must have come from the conversion of 2 Torr of alcohol, either directly or through acetone formation. The expected stoichiometries for those conversions are:

$$CH_3CH(OH)CH_3 + \tfrac{9}{2}O_2 \rightarrow 3CO_2 + 4H_2O \qquad (2)$$

and

$$CH_3COCH_3 + 4O_2 \rightarrow 3CO_2 + 3H_2O \qquad (3)$$

Clearly, there is a small inconsistency in the mass balance of the experimental data, since the total amount of alcohol consumed at the 20 min mark should add up

to 29 Torr, not the 27 Torr measured experimentally. However, all these values are within the error of our measurements, which is about 1–2 Torr.

Rough estimates for the rates of CO_2 formation were obtained from the slopes of traces, such as those in Fig. 5 between 30 and 55 min (after the maximum in acetone production is reached), and those were used to determine the rate law for CO_2 production, which was found to be approximately second-order with respect to P_{O_2}. This high order contrasts with the half-order reported for the production of acetone, and suggests that the selectivity for partial oxidation could be improved by maintaining the partial pressure of oxygen in the reaction low. An extreme example of this conclusion is illustrated by the data for the low oxygen pressures: at P_{O_2} below the stoichiometric value (15 Torr), no CO_2 production is detected at all. It was determined that the rate of CO_2 production also increases with the P_{O_2}/alcohol ratio when the oxygen partial pres-

sure is kept constant (data not shown). The rate of CO_2 production and total amount of CO_2 produced were found to increase with temperature as well. The activation energy for CO_2 formation was estimated at about 30 kcal/mol.

A series of independent experiments were carried out to determine the kinetics for the decomposition of acetone to CO_2 in order to separate the kinetics of oxidation of 2-propanol to acetone from its direct total oxidation to carbon dioxide. In a reaction mixture of 30 Torr of acetone with 15 Torr of oxygen, the rate of acetone consumption at 705 ± 2 K was found to be about the same as that for the mixture of 30 Torr 2-propanol with 30 Torr oxygen after the maximum conversion is reached (Fig. 6a), i.e. after all the alcohol has reacted and the fall in the acetone signal is observed. The rates of CO_2 formation in these two reactions are also comparable, see Fig. 6b. Notice that there is a delay in the production of CO_2 when starting
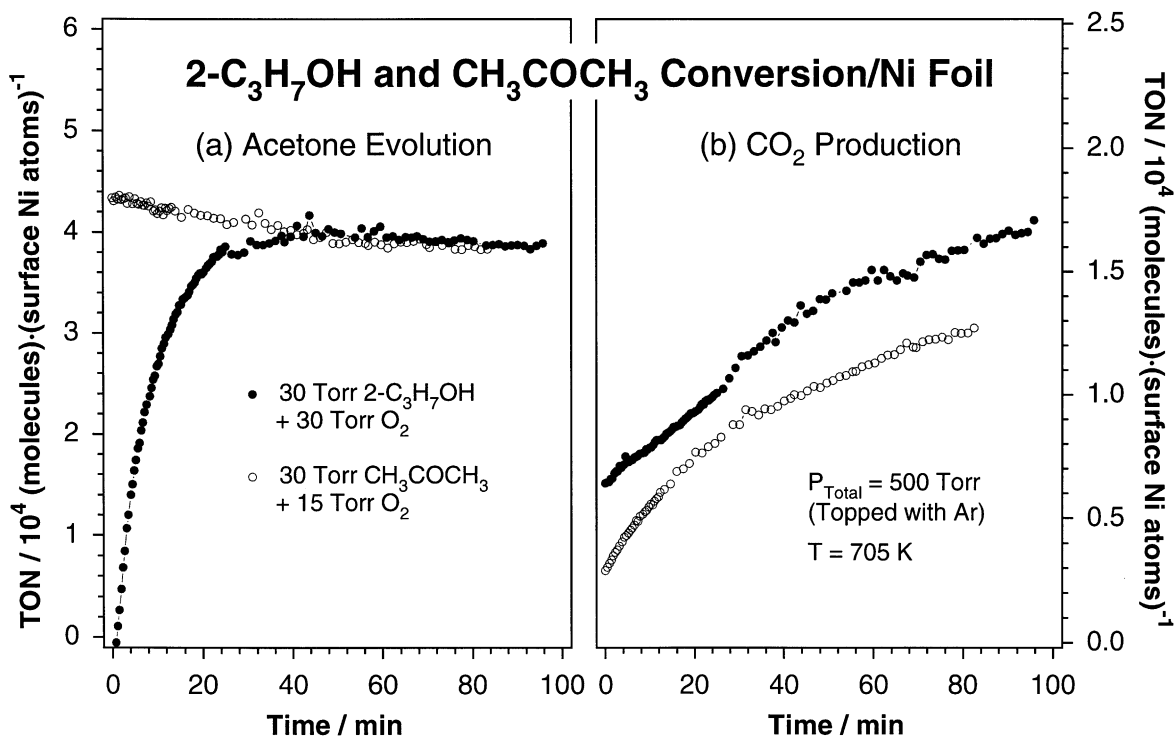

Fig. 6. Kinetics for the decomposition of acetone over a Ni foil at 705 ± 2 K. (a) Comparison between the time evolution of the decomposition of 30 Torr of pure acetone with 15 Torr of oxygen and that of the acetone formed from a 30 Torr 2-propanol + 30 Torr oxygen mixture. The two cases display comparable rates. (b) Comparison of the kinetics of CO_2 formation between the same two runs as in (a). Again, both sets of data indicate similar kinetic behavior when starting with the alcohol or with acetone.

with the alcohol, allegedly because of the prior need to produce acetone from the alcohol. No clear indication was obtained in our experiments for the direct conversion of the alcohol to CO_2; all the CO_2 produced could be accounted for by subsequent conversion of the acetone product. In terms of the stoichiometry of the acetone to CO_2 conversion reaction, the data from the experiments depicted in Fig. 6 indicate that about 13 Torr of oxygen (80%) reacts with ∼3 Torr of acetone. This corresponds to a reaction where about 4 mol of oxygen oxidize 1 mol of acetone, a ratio consistent with Eq. (3).

3.5. Nature of the surface of the catalyst during reaction

Finally, the role of surface oxygen in the mechanism of the oxidation of alcohols was explored. In particular, the importance of oxygen lattice atoms in those

reactions was assessed by performing kinetic experiments with nickel oxide films. As mentioned before, visible oxide films can be grown on the oxide foil via heating in 500 Torr of oxygen above 775 K. It was found that, in general, the rates for the formation of acetone and CO_2 are both higher on the O_2-pretreated surfaces (compared to those on clean nickel). An example of this is shown in Fig. 7 for the case of 30 Torr 2-propanol and 30 Torr of oxygen at 705 ± 2 K, and a more complete set of data is provided in Table 1 (where the calculated initial rates for acetone formation as a function of oxygen partial pressure are compared between clean and oxygen-precovered surfaces at 705 ± 2 K). The order of the acetone production reaction with respect to oxygen on O_2-pretreated surfaces was estimated to be 0.36 (as compared with the value of 0.51 on the clean nickel), and the average rate constant for acetone formation on the NiO film was calculated to be 42 ± 2 TOF/Torr$^{0.36}$ (molecules/Ni
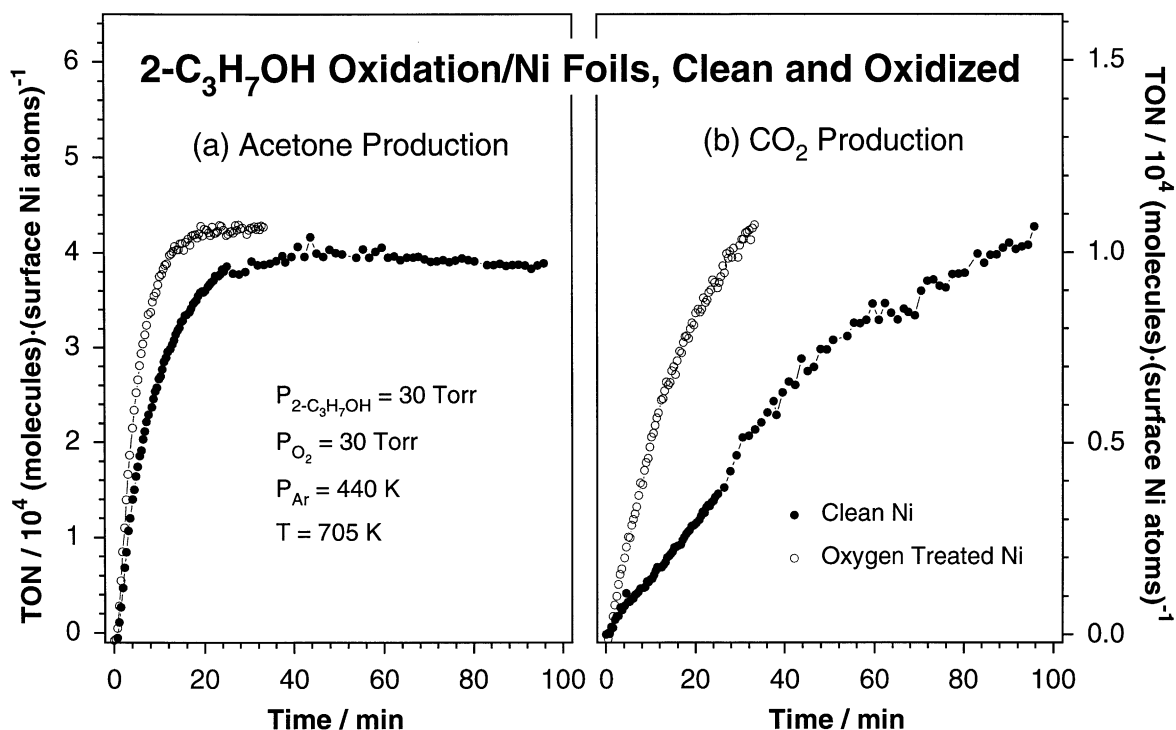

Fig. 7. Comparison of kinetic data for the oxidation of 2-propanol with oxygen between clean and oxygen-pretreated surfaces on nickel foils at 705 ± 2 K. Initial partial pressures of 30 Torr of 2-propanol and 30 Torr of oxygen were used in both cases. Panels (a) and (b) display the temporal evolution of acetone and carbon dioxide partial pressures, respectively. The rates of reaction for the formation of both products are higher on the oxide surface (also see Table 1), but the increase is more significant in the case of total oxidation. Similar behavior was observed with other reaction mixtures.
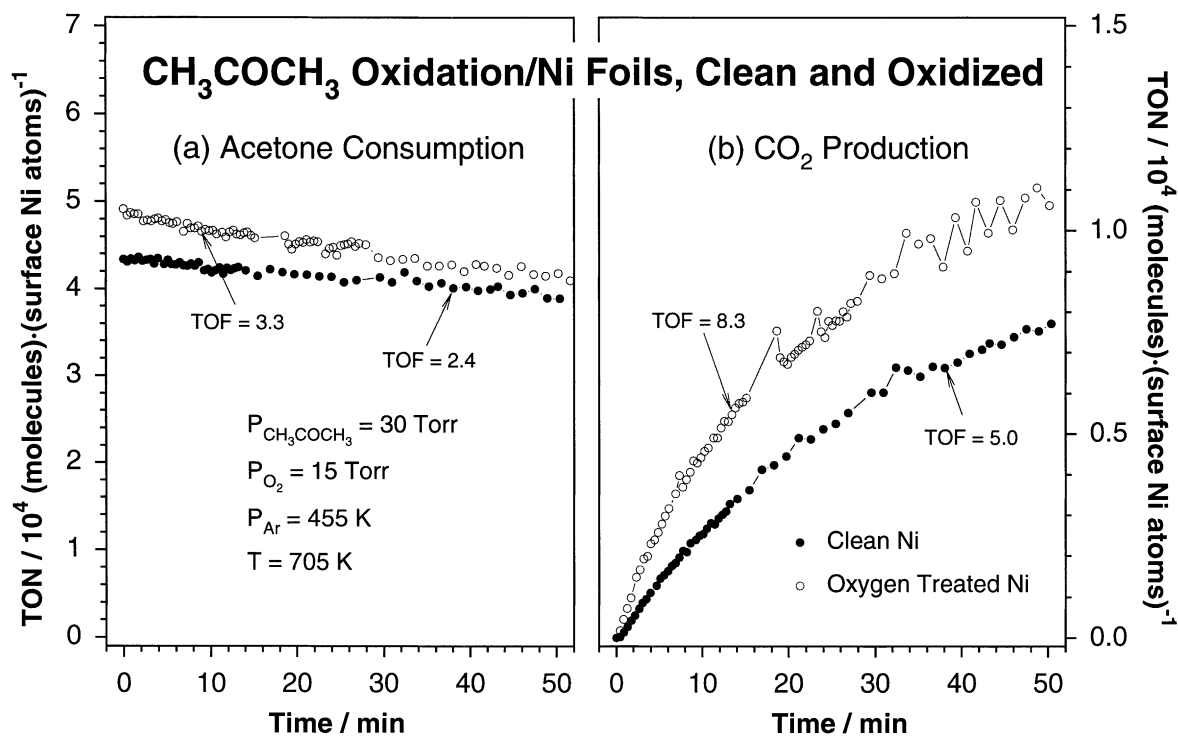
Fig. 8. Kinetics for the decomposition of acetone on clean and O_2-pretreated surfaces at $705 \pm 2\,K$. Panels (a) and (b) show the temporal evolution of the partial pressure of acetone and CO_2, respectively. The calculated initial rates are reported next to the corresponding traces.

atom s $Torr^{0.36}$), about three times that on the clean nickel.

In terms of selectivity, the maximum in acetone production on the nickel oxide surfaces reaches an approximately constant value of 84% with oxygen pressures equal to or higher than stoichiometric. This contrasts with the case of metallic Ni, where selectivities as high as 91% are possible (Table 1). The decrease in acetone relative yield in the oxygen-rich mixtures in going from metallic to oxidized Ni surfaces is due to the higher rates for acetone decomposition observed in the latter catalyst. The fact that the decomposition of acetone to CO_2 and water occurs at higher rates on Ni oxide surfaces is illustrated by the data in Fig. 8, which compares the time evolution of both the decomposition of acetone (a) and the production of CO_2 (b) on clean and oxygen-pretreated Ni catalyst for a mixture of 30 Torr acetone and 15 Torr oxygen. Initial rates, calculated the same way as in Section 3.2, are reported in that figure as well. It can be clearly observed from Fig. 8 that the decomposition of

acetone is comparatively faster on O_2-pretreated Ni surfaces. The dependence of acetone oxidation on oxygen partial pressure is also accentuated by surface oxidation: the rate of formation of CO_2 displays an order of about 2.4 with respect to P_{O_2} on O_2-pretreated Ni surfaces (versus 2.0 on the clean nickel). Lastly, some direct dehydrogenation of the alcohol to acetone and the formation of carbonaceous deposits are seen on oxygen-pretreated Ni surface at low oxygen pressures (i.e. 30 Torr of 2-propanol + 5 Torr of O_2), in an analogous way to the case of alcohol-rich mixtures on clean Ni.

An important feature of our experimental set-up is that it allows for the in situ visual observation of the changes that take place on the surface of the catalyst during the reactions. The build-up of either oxygen or carbon on the surface could be easily followed this way. Thin ($\sim$1000 Å) and uniform oxygen layers were seen to grow when heating the sample above 775 K in 500 Torr of oxygen for time periods as short as 1 min. As mentioned before, this oxide film developed on the

surface every time the sample was cleaned in oxygen, but was removed by the subsequent high-temperature hydrogen treatment. No oxide layers were visible at any point during the reactions carried out starting with a clean metal in our work, but that does not rule out the possibility that the nickel foil become covered by a very thin (∼10 Å) oxide layer during the alcohol oxidation reactions [49]; we believe that, because of the oxidative nature of the reactant mixture, the growth of an oxide-like thin film during the reaction is quite likely. On the other hand, carbon deposits were observed to grow as dark patches scattered on the surface after a few minutes of reaction in the alcohol-rich mixtures, and also when the stoichiometric mixtures were heated to higher (≥730 K) temperatures. The deposition of these carbonaceous deposits leads to both poisoning of the surface and the loss of electric conductivity through the sample, hence, the early stopping of the kinetic runs that ended up in the build-up of these surface species. The carbon deposits could be easily removed by heating the sample to 1000 K in 500 Torr of oxygen for a minute. Finally, carbonaceous layers are also deposited on the Ni oxide surface above 705 K in the presence of 30 Torr of pure alcohol. No acetone production was detected in that case, and no reduction of the oxide layer was seen either.

4. Discussion

4.1. Stoichiometry and selectivity on metallic nickel

The first conclusion that can be reached from our kinetic studies is that, as mentioned in Section 3.1, the stoichiometry of the oxidation of 2-propanol with molecular oxygen is such that 1 mol of the alcohol reacts with half a mole of oxygen to produce 1 mol of acetone and 1 mol of water (Eq. (1)). Evidence for this is provided by the data from the reaction of 30 Torr of 2-propanol with 15 Torr of oxygen, where the relative consumption of the alcohol and the oxygen were comparable at all times during the course of the reaction, and where both reactants were almost entirely consumed at $T = 705$ K after about 50 min. of reaction (Fig. 1). The same stoichiometry has been previously reported in the study of the photocatalytic production of acetone from 2-propanol and O_2 on Ti(1 1 0) [50].

One of the most important issues to consider when designing catalytic processes is the attainment of high selectivities toward the desired products. This is quite a challenge in the case of reactions between organic compounds and oxygen, since total oxidation is thermodynamically favored there. The selective production of partial oxidation molecules is still feasible, however, as long as the reaction is controlled kinetically and the desired products are extracted from the reaction mixtures. In the system studied here, the oxidation of 2-propanol by O_2, the product of interest is acetone, and the undesirable side reactions are the formation of carbon dioxide and hydrogen and, to a lesser extent, carbon monoxide and water. It was shown in this work that high selectivities toward acetone formation can be reached with nickel catalysts: Fig. 2 and Table 1 show that selectivities as high as 91% (27.3 Torr) towards acetone production are possible under the right settings, namely, at 705 K and with pressures of alcohol and oxygen of 30 and 60 Torr, respectively. In fact, it could be proposed that 100% selectivities could be achieved if the acetone were to be removed from the reaction mixture as soon as it is produced (see below). High selectivities have been reported in the past for 2-propanol conversion to acetone on oxidized anatase TiO_2 (95%) [51] and on Mn_3O_4 (85%) [52], both under atmospheric pressures.

It should be pointed out, however, that significant amounts of CO_2 are also produced under the conditions that optimize the production of acetone. Luckily, most of this CO_2 is formed after the point of maximum acetone conversion, as a comparison of Figs. 2 and 5 clearly demonstrates. Further analysis of the data in Fig. 5 also shows that the rate of CO_2 formation is initially low, and peaks only after the point of maximum conversion to acetone. These observations provide strong evidence for the sequential nature of the CO_2 formation reaction, i.e. for the fact that CO_2 is produced via the conversion of the acetone produced by alcohol oxidation, and not via direct oxidation of the initial alcohol. Another piece of evidence that supports this conclusion comes from the proportionality obtained between the integral of acetone pressure versus time curves and the CO_2 yield in the oxygen-rich mixtures (as expected if the rate of CO_2 formation is proportional to the partial pressure of acetone, plots not shown). Also, the rates for acetone decomposition and CO_2 formation from pure

acetone are comparable to those obtained directly in experiments with the alcohol (Fig. 6).

In terms of the reaction conditions required to optimize the selectivity toward acetone production, it is useful to notice that since the rate of alcohol oxidation to acetone is higher in the oxygen-rich mixtures (the rate is proportional to $P_{O_2}^{1/2}$), the maximum acetone production is reached at earlier times in those cases. However, since further decomposition of that acetone also accelerates with increasing O_2 pressures in the mixture, the maximum acetone yield is also affected by the composition of the mixture. According to the data in Table 1, the selectivity toward partial oxidation increases with P_{O_2}, at least up to a 60:30 oxygen-to-alcohol pressure ratio. On the other hand, the rate of formation of CO_2 shows a stronger dependence on oxygen pressure (that rate is proportional to $P_{O_2}^2$), which implies that P_{O_2} should be kept at values high enough to reach reasonable rates for acetone production but low enough to minimize any significant decomposition of that product. The sequential nature of the total oxidation process does facilitate this compromise.

Other side reactions should be taken into account as well. Some carbon monoxide production was detected in the experiments with mixtures of 30 Torr 2-propanol and either 30 or 60 Torr of oxygen, and also in those with 30 Torr of acetone and 15 Torr of oxygen (all at 705 K). The maximum amount of CO detected with $P_{ROH} = 30$ Torr and $P_{O_2} = 60$ Torr was about 3 Torr, which corresponds to the decomposition of about 1 Torr of the alcohol (or the acetone). Finally, direct dehydrogenation of 2-propanol to acetone in the absence of gas-phase oxygen is also possible on the nickel surface. This reaction, which most likely occurs via a direct β-hydride elimination step from a 2-propoxide intermediate [30,32,34,51,53,54], is slow compared to that in presence of oxygen (Fig. 2 and Table 1), displays only a weak dependence on temperature, and is accompanied by the production of hydrogen instead of water. This is easy to understand, given that the addition of oxygen to the reaction mixture makes the endothermic ($\Delta H = 13.7$ kcal/mol) conversion of 2-propanol to acetone become exothermic ($\Delta H = -44.1$ kcal/mol). In terms of selectivity, acetone formation directly via alcohol dehydrogenation is only important for alcohol-rich mixtures, and is undesirable anyway because it is accompanied by

significant total decomposition to carbonaceous deposits on the surface of the catalyst. It is quite possible for acetone formation in the presence of oxygen to also involve a β-H elimination step, and for such a reaction to be aided by the presence of surface oxygen, which could induce the formation of surface OH groups [31,34,44,51]. In terms of carbon deposition on the surface, that is likely to be due to direct complete decomposition of the alcohol, since, in absence of oxygen, heating pure acetone over the nickel catalyst leads to no change in the system.

4.2. Nature of the catalytic surface

Another factor to consider when designing and optimizing a catalytic process is the nature of the catalytic surface. In the system studied here the main issue in this context is the oxidation state of the surface nickel atoms under reaction conditions. In order to address this question, the oxidation of 2-propanol with oxygen was studied on both clean and O_2-pretreated Ni foils. The oxygen treatment used in our experiments resulted in the formation of an oxide film thick enough to be observable by visual inspection. This film was stable under our reaction conditions, and could not be reduced by the alcohol; only H_2 treatments at 1000 K could renew the metallic character of the surface. It was found (Section 3.5 and Fig. 7) that the rate of 2-propanol oxidation is significantly higher on this oxidized surface: in the case of acetone formation in particular, the data in Table 1 show a factor of about three difference between the two cases. Given that the reactions are carried out in a highly oxidizing environment, it is tempting to conclude that even when starting with clean Ni, the actual catalyst is always a nickel oxide film. If that is the case, however, such active oxide layer must be quite thin, because no characteristic oxide layer was observed by the naked eye during the reactions carried out in this work. The differences in activity and selectivity measured in the metallic and oxidized foils also argue for differences in the nature of the surface between the two cases. For instance, the maximum acetone yield on NiO is lower than on Ni, allegedly because the rate of acetone decomposition is also enhanced by the oxide layer on the surface (Fig. 8). It is, therefore, possible for two types of oxygen atoms to be present on the surface, the strongly-bonded lattice oxygen

associated with stable NiO films, and a more labile oxygen readily interchangeable with gas-phase O_2. The most likely scenario is that some form of atomic oxygen is involved in the rate-limiting step responsible for the acetone formation, but that this is not the lattice oxygen in NiO. Notice that when the alcohol is heated on the oxide surface by itself, without O_2, no acetone is produced, and no consumption of surface oxygen is observed either; the alcohol undergoes complete decomposition to carbon instead. Also, while gas-phase oxygen is likely to dissociate on the surface, it does not incorporate into the oxide lattice at the low temperatures of the reactions (this only happens with pure O_2 and above 755 K). We propose that the weakly adsorbed oxygen forms another reactive surface species, perhaps surface OH groups, instead.
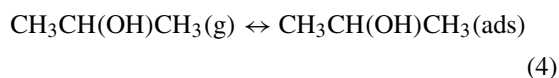
It has already been established in the past that oxygen chemisorbed on metal surfaces enhances the selective dehydrogenation of alcohols to aldehydes or ketones in ultrahigh vacuum conditions [19,30–32,34,44,45], even though the exact identity of this oxygen has not yet been determined. NiO lattice oxygen may influence the relative rate of the oxidation processes on the surface in our alcohol conversion experiments, but is not likely to directly participate in the hydrocarbon oxidation, because the NiO surface is never reduced to its metallic state during the reaction, and because gas-phase oxygen is necessary to promote the selective oxidation of 2-propanol to acetone. We believe that O_2 dissociative adsorption under the reaction conditions generate the reactive oxygen-containing species (perhaps OH groups) responsible for alcohol dehydrogenation.

4.3. Kinetics and mechanism for the oxidation of 2-propanol with molecular oxygen.
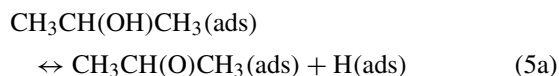
An important goal of this study was to elucidate the mechanistic details of the catalytic oxidation of alcohols on the nickel surface at the molecular level. Our study proved that, when starting with metallic nickel, the oxidation of 2-propanol by oxygen is approximately half-order with respect to molecular oxygen and zero-order with respect to the alcohol, and that the active catalyst involves some type of reactive thin oxygen-covered nickel layer. The independence of the reaction rate on the pressure of the alcohol can be thought as due to saturation of the surface

by that reactant, a hypothesis that also implies that most active sites may be blocked and not available for oxygen dissociation. This idea is supported by the fact that on the oxide surface, where poisoning of the surface by the alcohol is less significant, the reaction takes place at a faster rate. Moreover, the half-order in oxygen suggests the involvement of atomic oxygen in the rate-limiting step. Finally, the low apparent activation energy obtained here for the overall acetone production process, somewhere between 9 and 14 kcal/mol, suggests that this oxidation reaction may involve a hydrogen abstraction step. Based on these initial ideas and some additional information from the literature, the following mechanism is proposed:
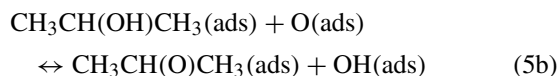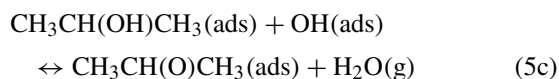
- Alcohol reversible adsorption:

$$CH_3CH(OH)CH_3(g) \leftrightarrow CH_3CH(OH)CH_3(ads) \tag{4}$$

- Alcohol dissociation to alkoxide:

$$CH_3CH(OH)CH_3(ads) \\ \leftrightarrow CH_3CH(O)CH_3(ads) + H(ads) \tag{5a}$$

or

$$CH_3CH(OH)CH_3(ads) + O(ads) \\ \leftrightarrow CH_3CH(O)CH_3(ads) + OH(ads) \tag{5b}$$

or

$$CH_3CH(OH)CH_3(ads) + OH(ads) \\ \leftrightarrow CH_3CH(O)CH_3(ads) + H_2O(g) \tag{5c}$$
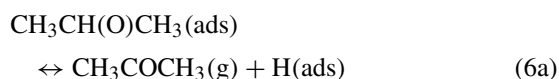
- β-Hydride elimination from 2-propoxide:

$$CH_3CH(O)CH_3(ads) \\ \leftrightarrow CH_3COCH_3(g) + H(ads) \tag{6a}$$

or

$$CH_3CH(O)CH_3(ads) + O(ads) \\ \rightarrow CH_3COCH_3(g) + OH(ads) \tag{6b}$$

or

$$CH_3CH(O)CH_3(ads) + OH(ads) \\ \leftrightarrow CH_3COCH_3(g) + H_2O(ads) \tag{6c}$$

- Water formation:

$$O_2 \text{ (g)} \leftrightarrow 2O\text{(ads)} \tag{7}$$

$$O\text{(ads)} + H\text{(ads)} \leftrightarrow OH\text{(ads)} \tag{8}$$
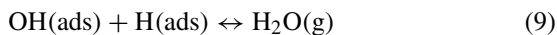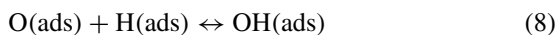
$$OH\text{(ads)} + H\text{(ads)} \leftrightarrow H_2O\text{(g)} \tag{9}$$
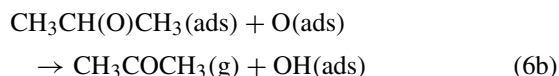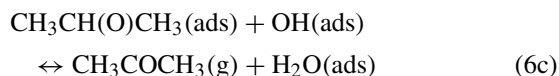
In the following paragraphs, we discuss these steps in more detail. First of all, the energy for Step 4, the reversible adsorption of the alcohol, is estimated to be $\Delta H_{ads} \sim -13$ kcal/mol based on the reported desorption temperature for 2-propanol on Pt(1 1 1) of 210 K [18] (similar values have been reported for other alcohols and other surfaces). Next, Steps 5a–c are believed to correspond to the first and fast reaction that occurs during the oxidation of alcohols on transition metal surfaces [17,19,4,31,32,53]. In fact, stable 2-propoxide intermediates have been isolated and characterized in a number of systems, both under ultra-high vacuum (UHV) [30,32,34,44,45,53,55], and at high pressures [51,52]. The possibility of the alkoxo hydrogen been abstracted by either O or OH groups on the surface is included in the mechanism presented here, but is not crucial for the understanding of the overall alcohol oxidation process because of the facile nature of this first dehydrogenation on all surfaces.

Steps 6a–c have also been clearly identified in surface science studies, and are believed to be rate-limiting, at least under vacuum [30,34]. Again, one issue connected with these steps is the role that atomic surface oxygen may play in facilitating the dehydrogenation reaction. Answering this question may not be important in the case of Steps 5a–c, but it is key in the evaluation of the overall reaction rates when discussing Steps 6a–c. The experiments reported here have clearly shown that Step 6a is indeed operative in these systems, but that it occurs at low rates compared to those when oxygen is present in the reaction mixture. In other words, it is clear that surface oxygen accelerates the second (β-H elimination) dehydrogenation step, most likely via Steps 6b and c. Direct evidence for this has also been previously provided in our surface science studies on the alcohol and alkyl/O–Ni(1 0 0) systems [34,44,45]. This point is important, because the intervention of oxygen-containing species in the abstraction of the β-hydrogen from the propoxide moiety accounts for

the rate dependence on oxygen pressure, as discussed below.

Finally, Steps 7–9, which account for the adsorption of oxygen and for water formation, have already been identified during the oxidative dehydrogenation of 2-propanol to acetone on O/Pt(1 1 1) [18], O/Pd(1 1 1) [32], and O/Cu(1 1 0) [31] surfaces. In our case, adsorbed oxygen is considered to be in equilibrium with gas-phase O_2. Oxygen adsorption on clean nickel is in fact mostly irreversible [56], but becomes weaker once the surface is passivated by an oxygen layer. As discussed in Section 4.2, we believe that in the nickel system the metal surface is partially passivated by the initial growth of an oxide-like thin film; this layer may facilitate the reversible dissociative adsorption of O_2. For reference, the energy of adsorption of O_2 on NiO has been reported to be about $\Delta H_{ads} = -11$ kcal/mol [57]. Our hypothesis of oxygen adsorption reversibility is also consistent with the quantitative evaluation of the activation energy, as discussed below.

Next, the mechanism proposed above is used to derive a rate law for the oxidation of the alcohol to acetone. If Step 6b is taken as the rate-determining step, the overall rate R for the alcohol oxidation reaction can be written as:

$$R = k_{6b}\Theta_O\Theta_{RO} \tag{10}$$

where Θ_O and Θ_{RO} are the surface coverages of oxygen and 2-propoxide, respectively. By using simple Langmuir adsorption expressions, the reversible nature of Steps 4 and 7, and a model of competitive adsorption between the alcohol and oxygen, the relevant coverages can be estimated as:

$$\Theta_O = \frac{K_{O_2}^{1/2} P_{O_2}^{1/2}}{1 + K_{ROH} P_{ROH} + K_{O_2}^{1/2} P_{O_2}^{1/2}} \tag{11}$$

and

$$\Theta_{ROH} = \frac{K_{ROH} P_{ROH}}{1 + K_{ROH} P_{ROH} + K_{O_2}^{1/2} P_{O_2}^{1/2}} \tag{12}$$

Now, assuming that the alcohol adsorbs more strongly than oxygen ($K_{ROH} P_{ROH} \gg K_{O_2}^{1/2} P_{O_2}^{1/2}$)

$$\Theta_O \sim \frac{K_{O_2}^{1/2} P_O^{1/2}}{1 + K_{ROH} P_{ROH}} \tag{13}$$

and

$$\Theta_{ROH} \sim \frac{K_{ROH}P_{ROH}}{1 + K_{ROH}P_{ROH}} \qquad (14)$$

Assuming that Step 5a is in equilibrium, as it is the case for methanol on Ni(1 1 0) [24] and Ni(1 1 1) [58], the concentrations of the alcohol and the alkoxide can be related by the expression

$$K_{5a} = \frac{\Theta_H \Theta_{RO}}{\Theta_{ROH}} \sim \frac{\Theta_{RO}^2}{\Theta_{ROH}} \qquad (15)$$

so

$$\Theta_{RO} = K_{5a}^{1/2}\Theta_{ROH}^{1/2} = \frac{K_{5a}^{1/2}K_{ROH}^{1/2}P_{ROH}^{1/2}}{(1 + K_{ROH}P_{ROH})^{1/2}} \qquad (16)$$

Finally, the reaction rate, Eq. (10), can then be written as:

$$R = \frac{[k_{6b}K_{5a}^{1/2}K_{O_2}^{1/2}K_{ROH}^{1/2}]P_{O_2}^{1/2}P_{ROH}^{1/2}}{(1 + K_{ROH}P_{ROH})^{3/2}} \qquad (17)$$

Rate expression 17 agrees reasonably well with our experimental finding. For one, it is consistent with the measured approximately half-order kinetics with respect to oxygen. Also, although the interpretation of the dependence of the reaction rate on alcohol pressure expressed by Eq. (17) is not as straightforward, it can also be made to agree with the experimental data. Specifically, notice that the order in P_{ROH} can be made to vary between -1 and $+1/2$ depending on the relative magnitude of $K_{ROH}P_{ROH}$ with respect to unity; our experimental value of 0.11 falls within that range.

In terms of the temperature dependence of the overall reaction rate, the empirical rate constant measured experimentally, k_{exp}, can also be directly related to the elementary steps in our mechanism by Eq. (17). For the extreme where the reaction is assumed to be half-order in the alcohol, this becomes:

$$k_{exp} = k_{6b}K_{5a}^{1/2}K_{O_2}^{1/2}K_{ROH}^{1/2} \qquad (18)$$

which leads to the expression:

$$E_{a,exp} = E_{a,6b} + \tfrac{1}{2}\Delta H_{5a} + \tfrac{1}{2}\Delta H_{O_2} + \tfrac{1}{2}\Delta H_{ROH} \qquad (19)$$

Fortunately, most of the energies in Eq. (19) can be extracted from temperature programmed data. $E_{a,6b}$ is estimated to be about 21 kcal/mol from thermal conversion data for either 2-propanol or 2-propyl

iodide on O/Ni(1 1 0) [34,44]. The activation energy for the forward Step 5a is estimated to be 10.4 kcal/mol from the adsorption of methanol on Ni(1 1 0) [24], and that for the corresponding reverse reaction about 15.2 kcal/mol [24]; ΔH_{5a} is, therefore, about -5 kcal/mol (by using a desorption temperature of 320 K for 2-propanol on O/Ni(1 1 0) [34,44], $\Delta H_{5a} \sim -8$ kcal/mol instead). Finally, ΔH_{O_2} and ΔH_{ROH} are taken to be -11 and -13 kcal/mol, respectively, as mentioned earlier. All this results a value for $E_{a,exp} \sim 6$ kcal/mol. At the other end, if in Eq. (17) it is assumed that $K_{ROH}P_{ROH} \gg 1$:

$$k_{exp} = k_{6b}K_{5a}^{1/2}K_{O_2}^{1/2}K_{ROH}^{-1} \qquad (20)$$

in which case the calculated activation energy comes out to be about 25 kcal/mol. For an approximately zero-order kinetics with respect to alcohol, as obtained under our experimental conditions, the activation energy would be expected to be somewhere between these two extremes, perhaps somewhere closer to 6 kcal/mol, and this is indeed the case: E_a was estimated in our experiments to be somewhere between 9 and 14 kcal/mol. It should be noted that if the adsorption of oxygen is assumed to take place over a clean metallic nickel surface, the heat of adsorption of that step would be around -120 kcal/mol [59], and that would lead to an unrealistically low activation energy of between -47 and -28 kcal/mol for the overall reaction (within the mechanistic assumptions made above).

Finally, if Step 6c is considered to dominate over Step 6b as the rate-limiting step (since surface OH groups are known to enhance the partial oxidation of 2-propanol to acetone [34]), the resulting rate law would be of the form:

$$R = \frac{[k_{6c}K_{5a}K_8K_{O_2}^{1/2}K_{ROH}]P_{O_2}^{1/2}P_{ROH}}{(1 + K_{ROH}P_{ROH})^2} \qquad (21)$$

where K_8 is the equilibrium constant for Step 8, for which $\Delta H = -16$ kcal/mol [60]; this would yield an estimated value for the overall activation energy of between -18 and 8 kcal/mol for the extreme first- and negative first-order kinetics in 2-propanol, respectively. Since the activation energy for the zero-order kinetics in alcohol based on these calculations does not completely agree with our measurement, it would appear that a mechanism in which Step 6b is the rate-limiting step (Eq. (17)) better accounts for the

temperature dependence of the rate measured in our experiments. It should be emphasized, however, that these kinetic arguments are not compelling enough to distinguish between the two possibilities (a particularly crude approximation of $\Theta_H \sim \Theta_{RO}$ was used to derive Eq. (15)), and that the activation energy range obtained if Step 6c is operative still almost includes the experimental value. Some of the surface science results do in fact lead to the idea that hydroxide surface groups are the likely intermediates in Step 6 [30,34,44]. All that can be said at this point is that the mechanisms supported by the experimental data in this report involve a reversibly adsorbed oxygen-containing species, either atomic oxygen or hydroxide groups.

4.4. Comparison with other systems

It has been shown in this study that high selectivities for alcohol conversion to acetone on Ni catalysts can be achieved by applying proper kinetic controls on that process, namely, by using O_2 pressures above stoichiometric and temperatures around 705 K. Our studies were carried out with a bulk nickel sample, but are likely to extrapolate to more practical supported catalysts, at least in the limit of low dispersion; this renders the alcohol/Ni system as promising for real catalytic applications. Again, the idea is not to use this specific process to produce acetone, but rather to extend it to other more interesting alcohol conversions. Preliminary results from our laboratory suggest that, indeed, the chemistry reported here for 2-propanol on nickel is quite general [61]. The mechanistic details of the oxidation reaction were provided here as well. This study follows some experimental findings from surface science work carried previously in our lab where the production of acetone via β-hydride abstraction from a 2-propoxide intermediate and the role of OH surface groups in accelerating this process were characterized in detail [34].

While high selectivities (up to 95%) for 2-propanol conversion to acetone have been reported in the past on oxidized anatase at atmospheric pressures, there is still some disagreement on the kinetic details of this dehydrogenation reaction due to the use of different samples among different groups [51]. Alcohol dehydrogenation was found to be enhanced by the addition of oxygen to the reaction mixture in some instances,

a result that agrees qualitatively with ours, but no order of reaction with respect to oxygen was reported in that system, so no direct comparison with our work is possible. Also, the acetone produced by thermal oxidation of 2-propanol with O_2 on titania was found to undergo fast decomposition to CO_2 and water [62]. On the other hand, the oxidation of adsorbed 2-propanol on a $TiO_2(1\,1\,0)$ single crystal by oxygen background was found to be almost insignificant unless light is supplied to the system [50]. In another example, an FT-IR study of the oxidation of 2-propanol on Mn_3O_4 by oxygen at atmospheric pressures reported an initial acetone yield of 85% at 523 K, but a subsequent drop to zero yield when the temperature was increased to 535 because of decomposition of the acetone to CO_2 [52]. No such marked increase in total oxidation reaction rates with temperature was observed in our system.

Of course, comparisons among different systems are limited by the different nature of the catalysts. Dehydrogenation of alcohols to aldehydes or ketones via direct β-H elimination has been reported over a number of late transition-metal surfaces [30,34,37,63,64]. In contrast, dehydration has been observed on some early transition metals [37]. Finally, dehydrogenation and dehydration compete on oxide surfaces such as $TiO_2(0\,0\,1)$ [38] and $ZnO(0\,0\,0\,1)$–Zn [39], where dehydration dominates, and $Cu_2O(1\,0\,0)$, where dehydrogenation prevails instead [65]. Changes in selectivity towards C–O bond-breaking steps may also be induced via surface modification [40], or by selection of the appropriate reactant [45,66,67]. Surface acidity seems to play a role in these changes in reaction selectivity, but, to the best of our knowledge, no systematic studies have been performed to explain all the observed results. What we can say at this stage is that nickel is a cheap candidate for selective alcohol dehydrogenation processes.

Some examples for the conversion of 2-propanol to acetone on oxygen-covered metal surfaces have been reported under UHV conditions as well [30–32]. In those studies, the surface oxygen coverage was found to critically control the selectivity toward acetone formation. Complete decomposition of the alcohol to H_2 and surface carbon dominates on clean metal surface and almost no reactivity is seen on oxide films; only at intermediate oxygen coverages some partial oxidation of the alcohol is observed. The rate of alcohol

decomposition was also found to be more significant in absence of oxygen in the present study, and the need to have gas-phase oxygen in the reaction mixture to replace the surface oxygen consumed was found to be critical in reaching high selectivities for the oxidation of 2-propanol to acetone, hence, the positive order of the rate on P_{O_2}. In addition, NiO was determined to be active under atmospheric conditions but to enhance total oxidation preferentially, another observation that matches that seen under vacuum. Finally, it appears from our catalytic work that NiO lattice oxygen is not involved in the formation of acetone, suggesting that this reaction occurs on nickel sites instead, and that it is helped by non-lattice oxygen surface species, probably OH groups. Once again, similar conclusions were reached by our previous surface science work.

5. Conclusions

Kinetic data were obtained for the selective oxidation of 2-propanol with molecular oxygen on clean and oxygen-pretreated Ni foils by using a microbatch reactor with mass spectrometry detection. High relative oxygen pressures and temperatures around 700 K were found to lead to high selectivities toward partial oxidation of the alcohol to acetone on both surfaces in the early stages of the reaction. Production of CO_2 was found to take place sequentially on the acetone produced by this first process. It was determined that, while the rate of the alcohol partial oxidation reaction is higher on the oxide, further decomposition of the resulting acetone is even faster on that surface, and that therefore, better selectivities are obtained when starting with metallic nickel. Approximately zero- and half-order kinetics with respect to 2-propanol and oxygen, respectively, were measured for the oxidation of 2-propanol to acetone on the clean Ni catalyst. This was interpreted by a mechanism where the preferential adsorption of the alcohol on the surface blocks the dissociative adsorption of the gas-phase oxygen. It was concluded that the oxygen atoms involved in the reaction are not the lattice oxygen in NiO, but rather a different more weakly adsorbed active oxygen species, possibly hydroxide surface groups. The rate-determining step of the overall acetone production is proposed to be the abstraction of hydrogen from a 2-propoxide intermediate by those active

oxygen species. The direct dehydrogenation of the alcohol via β-hydride elimination without the intervention of any surface oxygen is also possible, but occurs at a lower rate, and leads to further decomposition and to the growth of carbonaceous deposits on the surface.

Acknowledgements

References

[1] M. Mavrikakis, M.A. Barteau, J. Mol. Catal. A 131 (1998) 135.
[2] C. N. Satterfield, Heterogeneous Catalysis in the Industrial Practice, 2nd Edition, McGraw-Hill, New York, 1991.
[3] K. Weissermel, H.J. Arpe, Industrial Organic Chemistry, 2nd Edition, Verlag Chemie, Weinheim, 1993.
[4] J. March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, McGraw-Hill, Tokyo, 1968.
[5] G. Cainelli, G. Cardillo, Chromium Oxidants in Organic Chemistry, Springer, Berlin, 1984.
[6] W.A. Herrmann, J.P. Zoller, R.W. Fischer, J. Organomet. Chem. 579 (1999) 404.
[7] G.-J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, Science 287 (2000) 1636.
[8] K. Sakai, T. Ito, K.-I. Watanabe, Bull. Chem. Soc. Jpn. 39 (1966) 2230.
[9] M.E. Krafft, B. Zorc, J. Org. Chem. 51 (1986) 5482.
[10] M.E. Krafft, W.J. Crooks III, B. Zorc, S.E. Milczanowsky, J. Orgnomet. Chem. 53 (1988) 3158.
[11] T. Mukaiyama, T. Takai, T. Yamada, O. Rhode, Chem. Lett. (1990) 1661.
[12] T. Nishiguchi, F. Asano, J. Org. Chem. 54 (1989) 1531.
[13] I.M. Hoodless, R.A. Ross, R. Swaminathan, Can. J. Chem. 59 (1981) 865.
[14] Y.-F. Yao, J. Catal. 28 (1973) 139.
[15] S.G. Christoskova, N. Danova, M. Georgieva, O. Argirov, D. Mehandzhiev, Appl. Catal. A 128 (1995) 219.
[16] H. J. Schärfer, in: E. Steckhan (Ed.), Topics in Current Chemistry, Electrochemistry I, Vol. 142, Springer, Berlin, 1987.
[17] S.M. Gates, J.J.N. Russel, J.J.T. Yates, Surf. Sci. 171 (1986) 111.
[18] B.A. Sexton, K.D. Rendulic, A.E. Hughes, Surf. Sci. 121 (1982) 181.
[19] J.L. Davis, M.A. Barteau, Surf. Sci. 187 (1987) 387.

[20] J.B. Benziger, R.J. Madix, J. Catal. 65 (1980) 36.
[21] P.H. McBreen, W. Erley, H. Ibach, Surf. Sci. 133 (1983) L469.
[22] J. Hrbek, R.A. dePaola, F.M. Hoffmann, J. Chem. Phys. 81 (1984) 2818.
[23] J.E. Demuth, H. Ibach, Chem. Phys. Lett. 60 (1978) 395.
[24] S.R. Bare, J.A. Stroscio, W. Ho, Surf. Sci. 150 (1985) 399.
[25] S. Johnson, R.J. Madix, Surf. Sci. 103 (1981) 361.
[26] C. Houtman, M.A. Barteau, Langmuir 6 (1990) 1558.
[27] F. Solymosi, A. Berko, T.I. Tarnoczi, Surf. Sci. 141 (1984) 533.
[28] J.A. Gates, L.L. Kesmodel, J. Catal. 83 (1983) 437.
[29] N. Kizhakevarian, E.M. Stuve, Surf. Sci. 286 (1993) 246.
[30] X. Xu, C.M. Friend, Surf. Sci. 260 (1992) 14.
[31] P.D.A. Pudney, S.A. Francis, R.W. Joyner, M. Bowker, J. Catal. 131 (1991) 104.
[32] J.L. Davis, M.A. Barteau, Surf. Sci. 197 (1988) 123.
[33] S.W. Jorgensen, R.J. Madix, Surf. Sci. 183 (1987) 27.
[34] N.R. Gleason, F. Zaera, J. Catal. 169 (1997) 365.
[35] P.A. Dilara, J.M. Vohs, Surf. Sci. 321 (1994) 8.
[36] V.A. Gercher, D.F. Cox, J.M. Themlin, Surf. Sci. 306 (1994) 279.
[37] B.C. Wiegand, P. Uvdal, J.G. Serafin, C.M. Friend, J. Phys. Chem. 96 (1992) 5063.
[38] K.S. Kim, M.A. Barteau, J. Mol. Catal. 63 (1990) 103.
[39] J.M. Vohs, M.A. Barteau, Surf. Sci. 221 (1989) 590.
[40] C.W.J. Bol, C.M. Friend, J. Phys. Chem. 99 (1995) 11930.
[41] C.W.J. Bol, C.M. Friend, Surf. Sci. 364 (1996) L549.
[42] F. Zaera, Acc. Chem. Res. 25 (1992) 260.
[43] F. Zaera, J. Mol. Catal. 86 (1994) 221.
[44] N. R. Gleason, F. Zaera, in: R.K. Grasselli, S.T. Oyama, A.M. Gaffney, J.E. Lyons (Eds.), Proceedings of the 3rd World Congress on Oxidation Catalysis, San Diego, California, 21–26 September 1997, Elsevier Studies in Surface Science and Catalysis Series, Vol. 110, Elsevier, Amsterdam, 1997, p. 235.
[45] F. Zaera, N.R. Gleason, B. Klingenberg, A.H. Ali, J. Mol. Catal. A 146 (1999) 13.
[46] F. Zaera, Chem. Rev. 95 (1995) 2651.
[47] H.H. Kung, Adv. Catal. 40 (1994) 1.
[48] A. Loaiza, M. Xu, F. Zaera, J. Catal. 159 (1996) 127.
[49] J.C. de Jesús, P. Pereira, J. Carrazza, F. Zaera, Surf. Sci. 369 (1996) 217.
[50] D. Brinkley, T. Engel, J. Phys. Chem. B 102 (1998) 7596.
[51] J.E. Rekoske, M.A. Barteau, J. Catal. 165 (1997) 57.
[52] M. Baldi, F. Milella, G. Ramis, V.S. Escribano, G. Busca, Appl. Catal. A 166 (1998) 75.
[53] J.L. Davis, M.A. Barteau, Surf. Sci. 235 (1990) 235.
[54] Y. Shinohara, T. Nakajima, S. Suzuki, J. Mol. Struct. 460 (1999) 231.
[55] F. Zaera, J.M. Guevremont, N.R. Gleason, J. Phys. Chem. B 105 (2001) 2257.
[56] A. Bielanski, J. Haber, Oxygen in Catalysis, Marcel Dekker, New York, 1991.
[57] J. Haber, F.S. Stone, Trans. Faraday Soc. 59 (1963) 192.
[58] S.M. Gates, J.J.N. Russell, J.J.T. Yates, Surf. Sci. 159 (1985) 233.
[59] J.T. Stuckless, C.E. Wartnaby, N. Al-Sarra, S.J.B. Dixon-Warren, M. Kovar, D.A. King, J. Chem. Phys. 106 (1997) 2012.
[60] A.B. Anton, D.C. Cadogan, J. Vac. Sci. Technol. A 9 (1991) 1890.
[61] A. H. Ali, F. Zaera, 2001, to be published.
[62] S.A. Larson, J.A. Widegren, J.L. Falconer, J. Catal. 157 (1995) 611.
[63] R. Shekhar, M.A. Barteau, Catal. Lett. 31 (1995) 221.
[64] M.K. Weldon, C.M. Friend, Chem. Rev. 96 (1996) 1391.
[65] K.H. Schulz, D.F. Cox, J. Phys. Chem. 97 (1993) 647.
[66] X. Xu, C.M. Friend, Langmuir 8 (1992) 1103.
[67] N.F. Brown, M.A. Barteau, Langmuir 11 (1995) 1184.