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Kinetic study of the catalytic oxidation of alkanes over nickel, palladium, and platinum foils

Mansour Aryafar and Francisco Zaera*

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

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The kinetics of the total oxidation of alkanes (methane, ethane, propane, *n*-butane and isobutane) over Ni, Pd, and Pt foils was studied under fuel-lean conditions by using a recirculating batch reactor with mass spectrometry detection. Approximate first- and zeroth-order kinetics with respect to the hydrocarbon and oxygen concentrations, respectively, was observed in all cases. Significantly slower rates were seen for methane conversion, but other subtle changes were also identified among the other hydrocarbons as well. The reactivity trends could be clearly correlated with C–H bond strengths, since higher rates were seen for the longer and more branched hydrocarbon chains. Also, platinum was found to be the most active catalyst for the oxidation of all the compounds studied here except methane, which is oxidized faster on the nickel substrate. The variations in activity among the three catalysts were shown to be associated mostly with changes in the pre-exponential factor, not the activation energy, suggesting that they have to do with the surface density of active sites on the surface. The nature of the active catalyst during reaction was determined by simple inspection to be the metallic phase in the cases of Pt and Ni but an oxide layer in the case of Pd.

Keywords: total oxidation, alkanes, noble metals, kinetics, catalysis

1. Introduction

The catalytic total oxidation of hydrocarbons has been investigated in the past in connection with a number of practical applications such as hydrocarbon detection in enclosed environments [1,2], odor control [3], volatile organic compound removal from places such as polymer processing, coating operations, spray painting and offset printing [4,5], domestic [6,7] and other heating systems [8,9], industrial boilers [10], gas turbines [11–14], and fuel cells [15]. A renewed interest has surged in this area recently in connection with hydrocarbon emission control from both automobiles and power plants [16–19]. It was shown early on that noble metals, platinum and palladium in particular, are the most active for promoting oxidation reactions, so a large effort has been focused on studying catalysts based on those elements [1,20–23]. Moreover, given that methane constitutes more than 85% of the natural gas used in many modern combustion engines and that it is the most difficult alkane to burn, the majority of the work done over the last decade has targeted the palladium/methane system [24–39].

The kinetics and mechanism of the catalytic oxidation of hydrocarbons has indeed been studied extensively in the past. It has been found that the reaction rates usually display approximately zeroth and first order with respect to the partial pressures of oxygen and the hydrocarbon, respectively, especially under the fuel-lean conditions relevant to most pollution-control applications [5,20,22,40,41]. This rate law has been interpreted to be the consequence of an initial slow activation step for the hydrocarbon on an oxygen-covered surface, a point of particular importance given that the scission of the first C–H bond is still believed to occur on a metallic or nearly metallic site [23]. In fact, the nature of the active catalyst has been the subject of some controversy, but it is now widely agreed that, while platinum remains mostly in its zero valence state throughout the reaction, palladium owes its unique reactivity to the formation and participation of palladium oxide in the surface conversion steps; there seems to be some synergism between palladium metal and some form of PdO_x [31,32,37,38,42,43]. In addition, hydrocarbon oxidation over noble metals is structure-sensitive [27,28,44,45], and often displays induction periods [33,35], hysteresis [37,46], and aging [28]. Different explanations have been provided for this unique time-dependent behavior, but most argue for possible changes in either morphology or oxidation state of the palladium. Finally, the activity of the catalysts appears to be inhibited by the build-up of products (water and carbon dioxide) in the reaction mixture [33,47] and by halides [26,35].

Unfortunately, in spite of the great practical importance of hydrocarbon oxidation reactions, most work in this area has focused on a few specific systems, and there has been very little systematic basic research in terms of the active phase of the catalyst or the nature of the reactants. A few trends have nevertheless been reported already. For one, reasonably good correlations have been found between the ease with which the

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* To whom correspondence should be addressed.

alkanes are oxidized and the bond energy of their weakest C–H bond [23,40–42,48–50]. It has been clearly shown that the activation energy for the total oxidation of paraffins decreases with chain size, but it is not as clear if branching favors or hinders the reaction. The implication of this is, as mentioned above, that C–H bond activation is most likely the rate-limiting step of the whole process; this conclusion has been corroborated by isotopic substitution experiments, and it is widely accepted. In terms of the catalyst, noble metals have been proven much more active than oxides, but some contradictory reports can be found on the interdependence between reactivity and surface oxygen bond energy [20,22,51]. Also, platinum is recognized to be the most active material for the oxidation of most alkanes, but a higher reactivity has been reported repeatedly for palladium in the case of methane [33,41,42,44,50]. Other late transition metals (Rh, Ir, Ru) were found also to display high activities towards hydrocarbon oxidations [22,41], but almost no work has been published on nickel.

In this report we explore some of the points related to the catalytic oxidation of alkanes using noble metals enumerated above. The kinetics of the oxidation of the different C_1 to C_4 alkanes were measured over nickel, palladium, and platinum foils under fuel-lean conditions, and the activities of the solid samples were correlated with the pretreatments used for cleaning and with the nature of the surface before, during, and after reactions. It was found that the rate laws in all cases are approximately first order in the hydrocarbon and zeroth order in oxygen, the same as in other studies. Both reaction rates and activation energies were found to decrease with increasing chain size, but the effect of branching was not as obvious. Platinum was found to be more active than palladium in all cases, but, interestingly, nickel was shown to be more active than the other two metals for methane combustion. These differences in reactivity were shown to be related mostly with changes in pre-exponential factors, not activation energies, which means that they are likely to originate from changes in density of surface active sites in the catalyst. Also, the most active phases were identified by visual inspection to be the oxide for Pd and the metal in the cases of Pt and Ni.

2. Experimental

The experiments reported here were carried out in a recirculating batch reactor described in detail elsewhere [52]. Briefly, the stainless-steel loop and reactor, which has a total volume of 200 cm^3, is evacuated with a mechanical pump to a base pressure of about 5×10^{-3} Torr and then filled with the reacting gases (oxygen and the hydrocarbon) and topped off to a final pressure of 500 Torr by adding argon. The gases are mixed by using a recirculation bellows pump, and the time evolution of the partial pressures of the reactants and products is followed with a quadrupole mass spectrometer located in a separate chamber and connected to the reactor via a capillary tube. The collection and storage of data for further analysis is accomplished by using a personal computer interfaced to the mass spectrometer. Foils of about 8 by 12 mm^2 in area were used as catalyst samples. They were spot-welded to two tantalum bars connected to copper feedthroughs in order to allow for resistive heating, and their temperature was set by using an Eurotherm temperature controller and continuously monitored with a chromel–alumel thermocouple spot-welded to their back. Blank experiments were carried out both with contaminated samples and with gold and tantalum foils in order to ensure that the activity observed during the kinetic runs was entirely due to the noble metal being tested; propane oxidation with a tantalum sample was seen to start above 1100 K, a temperature approximately 450 K higher than when palladium was used instead. Lastly, a viewport was also available in the sample compartment for visual inspection.

The 15, 29, and 30 amu hydrocarbon peaks in their mass spectra were used to follow the partial pressures of methane, propane, and ethane, respectively, and the 58 amu signal was utilized for both *n*- and isobutane. The 18, 32, and 44 amu peaks were employed to follow the time evolution of the pressures of water, oxygen, and carbon dioxide, respectively, as long as there was no significant interference from the fragmentation of the hydrocarbons. The mass spectrometer signal intensities of the reacting gases were calibrated using a Baratron pressure gauge and converted to partial pressures. Rates and rate constants were then calculated afterwards by using the ideal gas law and the area of the foils. Finally, turnover numbers (TN) and turnover frequencies (TF) are reported in molecules per metal surface atom and in TN per second, respectively, and were estimated by assuming an atomic surface density of approximately 1.5×10^{15} metal atoms/cm^2.

The metal foils were purchased from Aldrich (99.9% minimum purity), and usually pretreated in situ before each reaction. The Pt and Ni samples were cleaned by successive exposures to oxygen and hydrogen at 1000 K, about 5 min each, and by then annealing to 1000 K under vacuum for a few minutes afterwards, and the Pd foils were treated the same way except that the reduction step was carried out with CO instead of H_2 to avoid palladium hydride formation. Additional pretreatments were explored for the cases of Pd and Ni, as discussed in more detail below. The gases were all purchased from Matheson, and used as supplied. All the hydrocarbons were of 99.5% minimum purity except for methane, which was 99.999% pure, and the oxygen, hydrogen, and argon were 99.999% pure as well.

3. Results

3.1. General procedures

The kinetics of the catalytic oxidation of several saturated hydrocarbons over Ni, Pd, and Pt foils were studied under fuel-lean conditions. Hydrocarbon partial pressure between 3 and 30 Torr and oxygen partial pressure between 60 and 300 Torr were used in most experiments. The reactivity of all three metal foils for the oxidation of each of the hydrocarbons was first investigated by a temperature-programmed oxidation method in which the extent of the conversion was followed as the temperature of the catalyst was ramped at a rate of about 5 K/min. Figure 1 shows a typical survey of conversion versus temperature for the case of the oxidation of 3.5 Torr of methane with 60 Torr of oxygen over a Pd foil. These data were used to determine an approximate light-off temperature (the inflexion point in the graph) and to choose the optimum temperature range to be used in subsequent isothermal kinetic studies. For instance, in the example in figure 1 the data show that methane conversion starts around 1050 K, lights off around 1115 K, and becomes too fast to be measured with our set-up by 1200 K; a temperature window between 1058 and 1178 K was therefore chosen for the isothermal measurements in this case. These results also indicate that the extent of methane conversion mirrors the amount of carbon dioxide formed, proving that the hydrocarbon undergoes stoichiometric total oxidation. This was true for all cases studied here (no other products were seen in the mass spectra of the gases).

Isothermal kinetic measurements were performed next. Figure 2 displays a representative isothermal catalytic run for the oxidation of methane over the Pd foil. A mixture of 3.5 Torr of methane and 80 Torr of oxygen was used in this case, and the reaction was carried out at 1178 K. This figure shows the evolution of the partial pressures of methane, oxygen, and carbon dioxide as a function of reaction time; the data for water was too noisy to be useful because of the high background pressure of this compound in the mass spectrometer. Note again that under the fuel-lean conditions used in these experiments the hydrocarbon combustion is stoichiometric and complete: the only products detected in these runs were carbon dioxide and water, and similar kinetic data were obtained by following the partial pressures of oxygen, carbon dioxide, and the hydrocarbon after accounting for the stoichiometry of the reaction (which

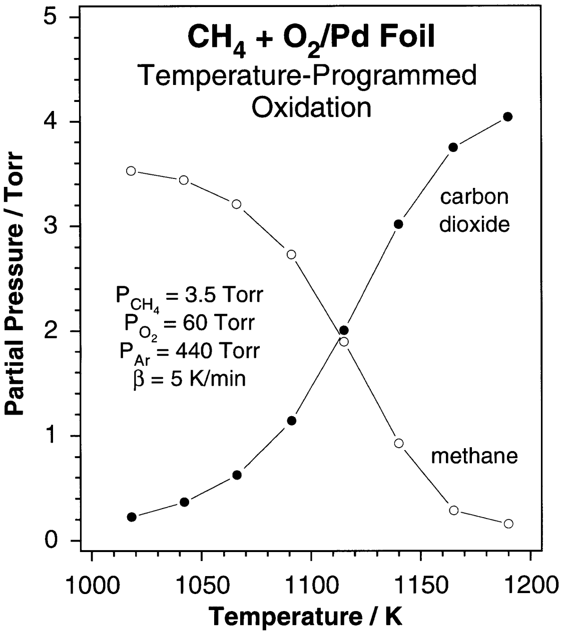

Figure 1. Data from a typical temperature-programmed oxidation (TPO) run for methane over a palladium foil under fuel-lean conditions. The recirculation micro-batch reactor was filled sequentially with 3.5 Torr of methane, 60 Torr of oxygen, and 440 Torr of argon, and the sample was then heated at a rate of 5 K/min while gas aliquots were taken periodically via a capillary tube and analyzed by using a mass quadrupole. This figure only displays the temporal evolution of the partial pressures of methane and carbon dioxide, but those of water and oxygen were followed as well; no other compounds could be detected in the gas phase. A light-off temperature of about 1115 K was measured in this case. Similar experiments were performed for all the hydrocarbons and all the metals employed in this study (see text).

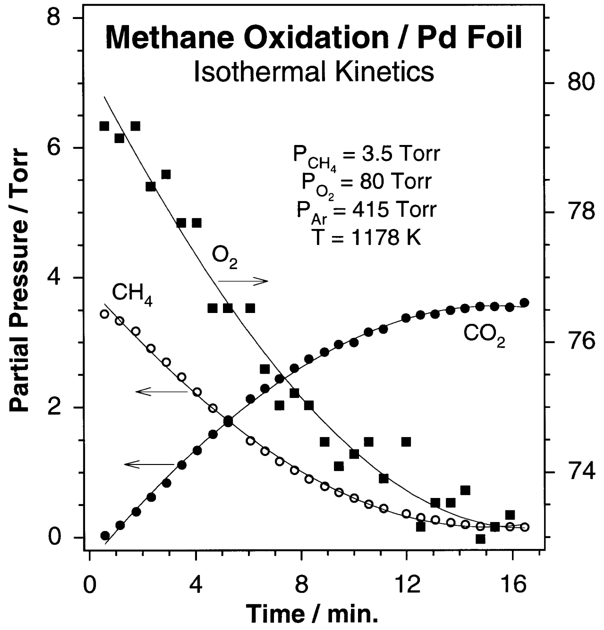

Figure 2. Results from a typical isothermal kinetic run for the oxidation of alkanes on metal foils using our experimental set-up. The case presented here is that of the conversion of 3.5 Torr of methane and 80 Torr of oxygen over a palladium sample. The total pressure of the reactor loop was taken up to about 500 Torr with argon in order to facilitate the operation of the recirculation pump, and the solid was then heated to a constant temperature of 1178 K by using a commercial controller. Periodic gas samples were analyzed by mass spectrometry via a capillary tube, the same as in the TPO experiments. Shown in this figure is the temporal evolution of the partial pressures of methane, oxygen, and carbon dioxide; the pressure of water, the other product, was difficult to follow because of the high background signal in the vacuum chamber hosting the mass spectrometer.

in this case is $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$). Since the data for the rate of disappearance of the hydrocarbon usually had the least noise, those are the ones reported in the remainder of this paper.

Reaction rate constants were calculated from data such as those in figure 2 by either one of the two methods illustrated in figure 3. In one (left panel of figure 3) initial rates were estimated first from the slope in the pressure versus time plots at early times (but after the first couple of minutes, because there is an induction period due to the delay induced by the slow diffusion of the gas sample into the mass spectrometer), and rate constants k were then calculated by dividing those numbers by the initial hydrocarbon partial pressure. The second approach is based on using first-order kinetics, by assuming that the rate is proportional to the partial pressure of the hydrocarbon (see below). Such rate law makes semilogarithmic plots such as that in the right panel of figure 3, of $\ln[P^0_{HC}/P_{HC}]$ vs. time, yield a straight line with a slope which corresponds directly to k. The two approaches described in this paragraph yielded similar results for k.

3.2. Determination of kinetic parameters

The pressure dependence of the reaction rates for the oxidation of each of the alkanes on all three metals was determined first. An example of the results from those studies is given in figure 4, which depicts data for the case of *n*-butane oxidation over Ni foils. The changes in the initial turnover frequency as a function of the partial pressures of the alkane (left) and oxygen (right) were plotted here in a log–log manner in order to extract reaction orders (which are given directly by the slope of those graphs). In most cases a constant oxygen pressure of 60 Torr was used in the first set of experiments as the pressure of the hydrocarbon was varied from 1 to 5 Torr, and the alkane pressure was fixed at 3 Torr while the oxygen pressure was changed from 20 to 100 Torr in the second. In all cases it was found that the rate law for the oxidation is described at least approximately by first-order kinetics with respect to the concentration of the hydrocarbon and zeroth-order dependence with respect to the concentration of oxygen, in agreement with previous reports [5,20,22,40,41]. These rate laws were also corroborated by the linearity of plots such as that in the right panel of figure 3. Small differences were nevertheless observed among the individual cases, specially as far as the oxygen pressure dependence is concerned (table 1). For instance, a small positive order, on the order of 0.2–0.4, was measured for most hydrocarbons on nickel, while on platinum and palladium the dependence was often mildly negative. These differences may not be significant because they may be related to the temperature at which the pressure-dependence kinetic studies were carried out and that had to be chosen for each hydrocarbon–metal combination based on its specific reactivity behavior; although all surfaces are expected to be almost completely covered with oxygen under the fuel-lean conditions used here, the actual oxygen coverage may be affected by the reaction temperature. This is a point worth exploring in more detail, since it can shed more light into the nature of the active site for the initial alkane activation step [49,51].

Isothermal kinetic measurements were also carried

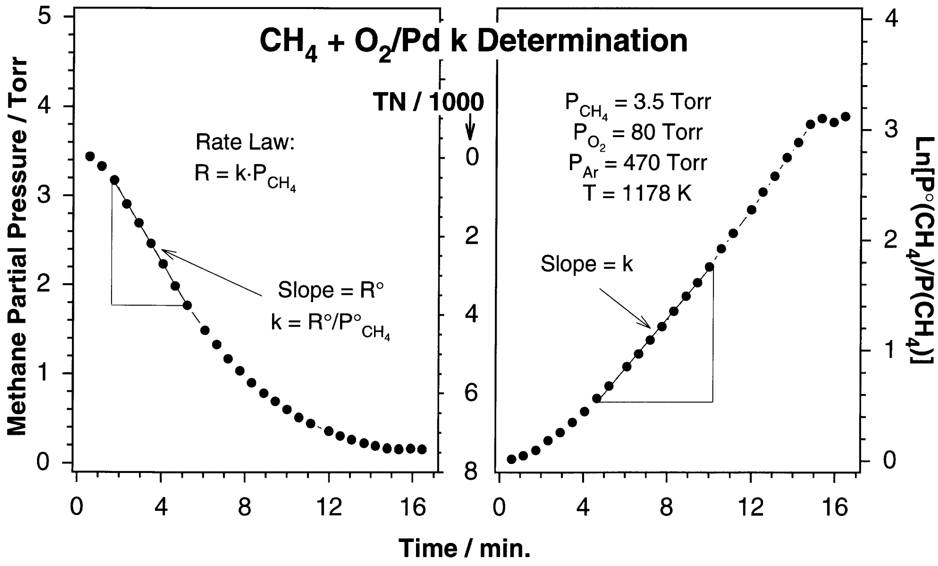

Figure 3. Illustration of the procedures followed to calculate reaction rate constants (k) from isothermal kinetic data such as those shown in figure 2. Left: methane partial pressure versus time for the reaction between 3.5 Torr of methane and 80 Torr of oxygen over a palladium foil at 1178 K. The slope of the initial decay was divided by the initial partial pressure of the hydrocarbon to estimate the value of k. Right: semilogarithmic plot of the same data as in the left. Since the rate laws for most oxidation reactions are first order in the hydrocarbon and zeroth order in oxygen (see figure 4 and text), these semilogarithmic plots yield (after a small induction period associated with the sample delay in our instrument) straight lines, the slopes of which provide the value of k directly.

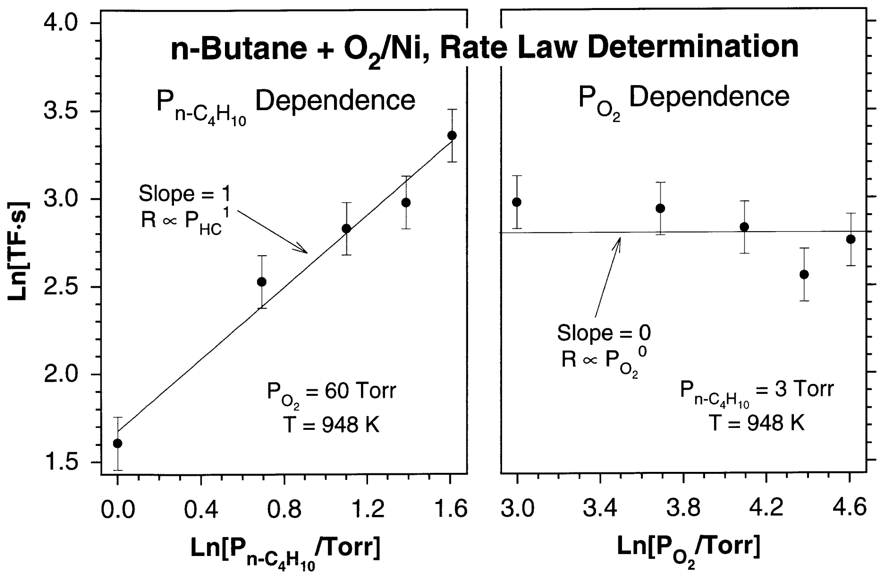

Figure 4. Pressure dependence studies for the oxidation of *n*-butane with oxygen over a nickel foil. Left: the pressure of the hydrocarbon was varied from 1 to 5 Torr while that of oxygen was kept at 60 Torr to determine the approximately linear dependence between the reaction rate and the concentration of the *n*-butane. Right: the partial pressure of oxygen was varied between 20 and 100 Torr while keeping that of *n*-butane constant at 3 Torr in order to show the nearly independence of the rate on oxygen concentration in this pressure regime. All these experiments were carried out at a total pressure of 500 Torr (by using argon as the ballast gas) and a foil temperature of 948 K. Experiments with other alkanes and metal foils yielded similar results (table 1).

out as a function of temperature for all the alkanes and all the metals studied here. The results obtained for the rate constants are reported in Arrhenius plots in figure 5, and the kinetic parameters, namely, the activation energies and pre-exponential factors calculated from those data, are summarized in table 2. Notice that there is a “rollover” at the high temperature end of some of the plots, in particular for the case of platinum, but even though a similar behavior has been reported previously [49], we believe that in our case this may be the result of a limitation in the rates that can be measured with our experimental set-up (because of mass-transfer limitations in the capillary to the mass spectrometer). Otherwise the kinetic parameters reported here do in general follow the expected trends in terms of the structure of the hydrocarbon, that is, the activation energies decrease with chain length. The energy barrier is particularly high for methane, for which a value of about 30 kcal/mol was measured here on all three metals. This is in agreement with most studies, although numbers between 18 and 48 kcal/mol have been reported in the literature [1,20,33,44,45]. Good agreement was also found between the data obtained here for the other hydrocarbons and previous work in spite of the fact that significant deviations are evident among the different reports (table 3): there is a particularly good match between our data and those of Hiam et al. [48] for platinum, and not as good but still acceptable agreement with the results of Cullis et al. [49] for palladium. In terms of the pre-exponential factors, they were seen here to decrease with alkane size for nickel and palladium, but to go through a maximum in the case of platinum; their values cover the

Table 1

Parameters for the rate laws in the total oxidation of light paraffins on nickel, palladium, and platinum foils under fuel-lean conditions. The rate is expressed by the empirical relationship $R = kP_{HC}^{a}P_{O_2}^{b}$. The reaction conditions used were as follows: for Ni and Pd, P_{HC} was varied between 1 and 5 Torr while keeping P_{O_2} at 60 Torr, then P_{O_2} was varied between 20 and 100 Torr while keeping P_{HC} at 3 Torr; for Pt the same conditions were used for all hydrocarbons except methane and ethane, for which P_{HC} was varied between 10 and 30 Torr while P_{O_2} was kept at 300 Torr, and then P_{O_2} was varied between 100 and 300 Torr while keeping P_{HC} at 10 Torr. The volume of the reactor was always taken to a total pressure of 500 Torr by using argon as the ballast gas

	Nickel			Palladium			Platinum		
	T (K)	*a*	*b*	*T* (K)	*a*	*b*	*T* (K)	*a*	*b*
methane	928	0.9 ± 0.1	0.2 ± 0.1	1178	1.0 ± 0.1	−0.1 ± 0.1	1073	1.1 ± 0.1	−0.1 ± 0.1
ethane	973	0.9 ± 0.1	0.3 ± 0.1	833	1.0 ± 0.1	−0.1 ± 0.1	973	1.0 ± 0.1	0.0 ± 0.1
propane	973	0.8 ± 0.1	0.3 ± 0.1	753	1.0 ± 0.1	0.0 ± 0.2	873	1.2 ± 0.1	−0.2 ± 0.1
n-butane	948	1.0 ± 0.2	−0.2 ± 0.2	688	1.0 ± 0.1	0.0 ± 0.2	673	1.2 ± 0.1	−0.2 ± 0.1
isobutane	943	0.7 ± 0.3	0.4 ± 0.3	718	1.1 ± 0.1	0.0 ± 0.2	673	1.3 ± 0.1	0.2 ± 0.1

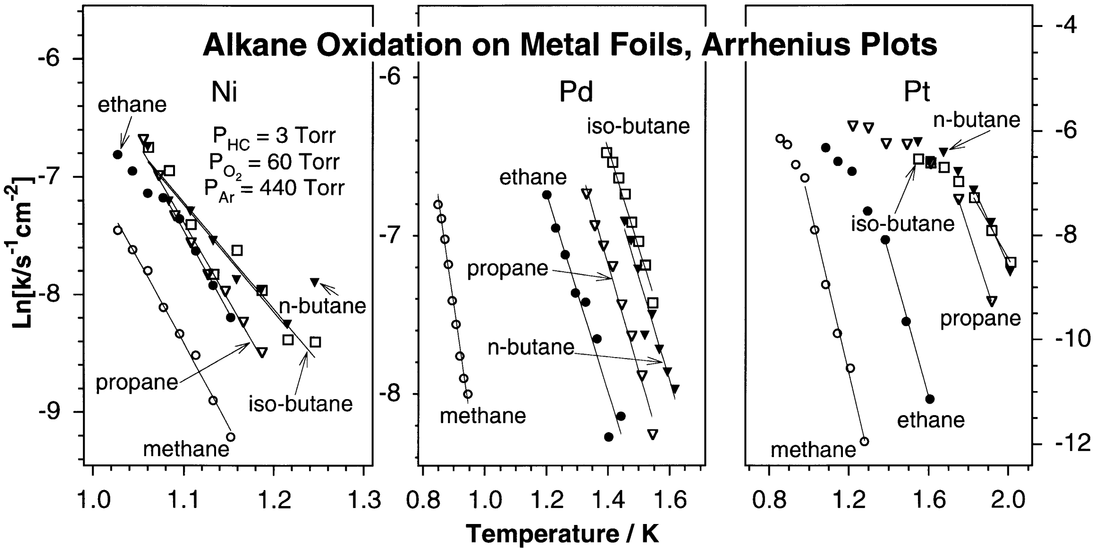

Figure 5. Arrhenius plots for the oxidation reaction between alkanes (methane, ethane, propane, and *n*- and isobutane) and oxygen on all three metals (nickel, palladium, and platinum) studied here. Each value of *k*, the reaction rate constant, was determined by isothermal experiments such as those illustrated in figures 2 and 3. The activation energies and pre-exponential factors resulting from this analysis are summarized in table 2.

range between 1×10^{-15} and 3×10^{-10} per surface atom and second. Comparison with other work in this case is not easy because of the different ways the pre-exponential factor is calculated, but the similar ignition temperatures [42,48] or temperature ranges [41,49] reported before are an indication of the similarity with our kinetics.

The trends in reactivity are better highlighted by temperature-programmed oxidation experiments such as those described in the previous section. The changes seen for a given metal towards different hydrocarbons were probed first; figure 6 displays the sequence obtained for the Pd foil. It was found that on that metal methane oxidation starts around 1060 K, while the other compounds (ethane, propane, *n*-butane, and isobutane) ignite at temperatures around 700 K; on Pt the values are approximately 900 K for methane and 500–570 K for the others, and on Ni all the alkanes burn at slightly above 800 K. Again, methane is always much harder to burn than the other paraffins, and the ease with which the other compounds are converted increases with hydrocarbon chain size.

The variations in activity induced by changing metals are exemplified in figure 7. For all hydrocarbons other than methane the ease with which they are oxidized follows the sequence Pt > Pd > Ni, but, interestingly, in the case of methane it was found that nickel is the most effective catalyst for this reaction. It is important to point out in connection with this switch that nickel behaves in a unique manner because: (1) there is not much difference in reactivity for that metal between methane and the other alkanes; (2) the temperature-programmed oxidation curves obtained with Ni do not display the nice sigmoidal shapes seen for the other two metals; and (3) the isothermal runs display a noticeable deviation from first-order kinetics with time. This latter observation was accompanied by the slow build-up of a nickel oxide film on the surface (see below). We therefore propose that the active phase in the nickel case is the metal, and that its activity decreases with time as a con-

Table 2

Activation energies and pre-exponential factors for the total oxidation of light paraffins on nickel, palladium, and platinum foils under fuel-lean conditions. The reaction conditions used were as follows: for Ni and Pd, $P_{HC} = 3$ Torr, $P_{O_2} = 60$ Torr, and $P_{Ar} = 440$ Torr; for Pt, $P_{CH_4,C_2H_6} = 30$ Torr, $P_{C_3H_8} = 5$ Torr, and $P_{C_4H_{10}} = 3$ Torr, $P_{O_2} = 300$ Torr for CH_4 and C_2H_6 and 60 Torr for C_3H_8 and C_4H_{10}, $P_{Ar} = 170$ Torr for CH_4 and C_2H_6, 440 Torr for C_3H_8 and C_4H_{10}

	Nickel			Palladium			Platinum		
	T range (K)	E_a (kcal mol^{-1})	*A* (s^{-1} cm^{-2})	*T* range (K)	E_a (kcal mol^{-1})	*A* (s^{-1} cm^{-2})	*T* range (K)	E_a (kcal mol^{-1})	*A* (s^{-1} cm^{-2})
methane	868–973	28.1	1300	1058–1178	26.7	100	782–1173	32.1	6600
ethane	868–973	27.8	2700	693–833	12.4	2	573–973	27.3	54000
propane	843–948	26.5	1500	648–753	13.4	10	523–873	23.3	540000
n-butane	803–943	18.2	20	618–688	13.0	10	498–673	17.0	4900
isobutane	803–943	18.0	20	648–718	12.5	10	498–673	13.4	150

Table 3
Comparison between the activation energies obtained here for the oxidation of hydrocarbons on noble metals and those reported previously. All values are given in kcal/mol

Reference	Catalyst	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	iso-C_4H_{10}
	palladium					
this work	foil	26.7	12.4	13.4	13.0	12.5
[49]	on Al_2O_3 beads	13.4	20.1	15.6	–	11.0
[41]	wire	17	22	23	26	–
[50]	black	14.4	–	–	23.9	–
	platinum					
this work	foil	32.1	27.3	23.3	17.0	13.4
[48]	filament	–	27.3	17.0	17.0	10.2
[41]	wire	21	26	22	25	–
[50]	black	28.2	–	–	19.1	–

sequence of site blocking by the growing NiO coating. It could be thought that steam reforming may play a role in the nickel case, but this is unlikely because no CO was detected by mass spectrometry at any point during the kinetic runs.

3.3. *Effect of sample pretreatment on the reaction kinetics*

Complementary experiments were performed by varying the pretreatment used to clean the metal foils before reactions in order to identify the active phase of the catalyst. Four different pretreatment sequences were tested here: (1) a quick flash of the surface to 1000 K in vacuum before reactions; (2) exposure of the foil to 500 Torr of oxygen at 1000 K for about 5 min prior to flashing to the same temperature under vacuum; (3) sequential 5 min treatments with 500 Torr of oxygen and 500 Torr of hydrogen, both at 1000 K, and then pumping of the system; and (4) sequential 5 min 500 Torr treatments with oxygen and carbon monoxide at 1000 K followed by pumping.

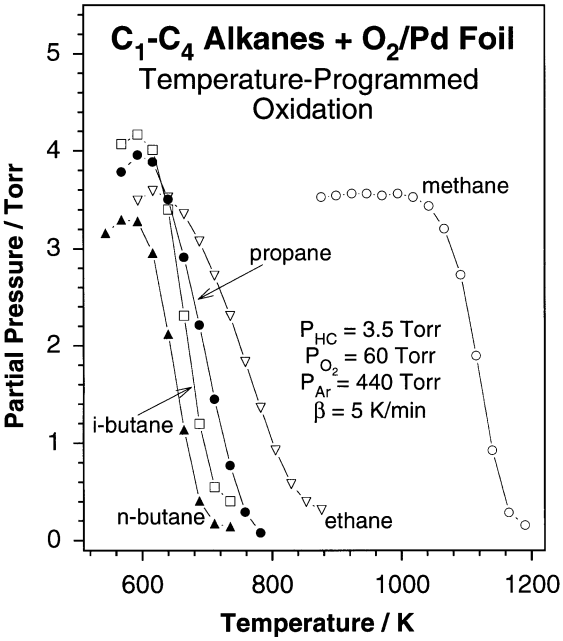

Figure 6. Temperature-programmed oxidation data for the different alkanes on a palladium foil. All these experiments were carried out by using 3.5 Torr of the hydrocarbon, 60 Torr of oxygen, and 440 Torr of argon, and by heating the foil at a rate of 5 K/min. A clear trend is seen in this figure in terms of reactivity, as indicated by the shifts down in light-off temperature seen with increasing hydrocarbon chain size. This represents a direct correlation between the ease of oxidation of the paraffin and the bond energy of its weakest C–H bond.

An indication of the nature of the catalyst both after the different pretreatments and all throughout the kinetic reaction runs was provided by the physical appearance of their surfaces. In the case of palladium the initial foil was shiny and of a metallic silvery color in spite of the likelihood that the surface was covered by a thin layer of contaminant hydrocarbons. Upon oxidation, however, that substrate turned greenish-blue, indicating the formation of palladium monoxide (PdO) [53]. After exposure to hydrogen the foil then appeared to swell as it formed the palladium hydride (Pd_2H), and it turned silvery gray (dull instead of shiny), became quite brittle, and never recuperated its shine again. Because of the significant physical changes induced by this latter treatment, the foils exposed to hydrogen were not used for any measurements other than those discussed in this section. Lastly, reduction of the oxide with CO instead of hydrogen did reverse the sample to its shiny metallic state.

The behavior of the palladium foil during the formation of water induced by the oxygen + hydrogen treatments was investigated in a bit more detail. When hydrogen was added to an oxygen-pretreated palladium foil, its color was seen to change from greenish-blue (PdO) to silvery gray (as mentioned above), the temperature was seen to increase by about 60–70 K without any external heating, and large amounts of water were detected by the mass spectrometer. When oxygen was added to a hydrogen-pretreated palladium, on the other

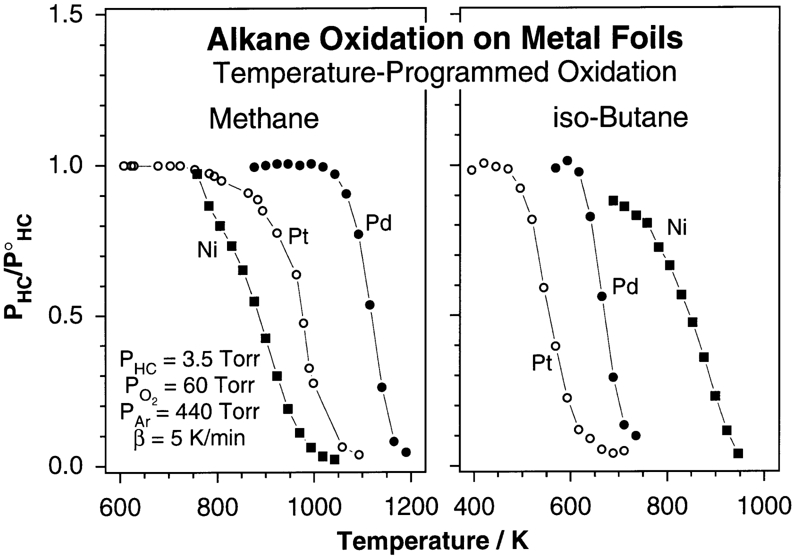

Figure 7. Temperature-programmed oxidation data for methane (left) and isobutane (right) on all three (Ni, Pd, and Pt) foils. All the experiments were carried out by using 3.5 Torr of the hydrocarbon, 60 Torr of oxygen, and 440 Torr of argon, and by heating the foil at a rate of 5 K/min. Platinum proved to be the most active catalyst for the oxidation of all the hydrocarbons used here other than methane, but methane was shown to burn at lower temperatures on the nickel foil.

hand, the color of the surface changed from silvery gray (Pd_2H) back to greenish-blue (PdO), but significantly less water was produced, and the temperature rise of the foil was an order of magnitude larger (about 600–700 K). The difference in the temperature jumps seen in both cases is most likely explained by the differences in the amount of the heat released during PdO formation, which is about −20.4 kcal/mol [53], as compared to that from Pd_2H formation, which amounts to only −8.9 kcal/mol [53].

The catalytic activity towards hydrocarbon total oxidation of the pretreated Pd foils was then probed at 753 K by using 3 Torr of propane and 60 Torr of oxygen. Also, several runs were performed for each type of pretreatment in order to evaluate the reproducibility of the treatments. This was needed because it was found that it usually took between 5 and 15 cycles for the sample to behave in a predictable manner. Figure 8 displays some of the key results obtained for the propane oxidation rate constants on Pd (and Ni) foils after the different pretreatment procedures: the hatched bars provide the lower limit for the value of k, and the white bars on top represent the spread obtained in the reproducibility experiments. It can be seen in this figure that for the case of palladium the oxygen + CO pretreatment is clearly the most effective in terms of both activity and reproducibility. It was also seen that the palladium hydride does not remain in that state but converts into the (non-crystalline) metal during the early stages of the reaction, and that the resulting sample can still catalyze hydrocarbon oxidations with the same efficiency as a new foil. Indeed, when the reaction is started by heating the hydride to 753 K in the presence of the reaction mixture, the color of the foil changes almost immediately from silvery gray (Pd_2H) to greenish-blue (PdO), the same as when exposing it to oxygen alone. The greenish-blue sample color was in fact seen during the course of the reactions in all cases, suggesting that palladium monoxide is the active species which catalyzes the hydrocarbon oxidation [20,33,49,50]. Interestingly, at the end of the reaction, after all the hydrocarbon molecules were oxidized, the foil heating was turned off to allow it to cool down, and the gases were pumped out, the color of the foil became a dull red indicative of palladium dioxide ($PdO_2 \cdot xH_2O$) formation.

Additional reproducibility experiments were designed to check for self-poisoning during the oxidation of propane over the Pd foil. The initial conditions were kept identical to those used before, namely, the reactions were started at 753 K by using a mixture of 3 Torr of propane and 60 Torr of oxygen, but the reactor was then evacuated after a preset reaction time (about 5, 10, 15, 20, and 25 min) while keeping everything else unchanged (and maintaining the sample at 753 K), and then refilled with new reactants soon after. In these kinetic experiments the reaction was seen to pick up right from the start at the same rate as the initial run, and 100% conversion of the second mixture was obtained in the expected time interval. This indicates that the operating surface of the catalyst is not modified by the reaction mixture under the conditions used here.

Similar kinetic experiments following the different pretreatment procedures were performed for the oxidation of propane on nickel at 873 K (figure 8). In the case of the original Ni sample, after only flashing to 1000 K, the foil eventually changed in color during the reaction,

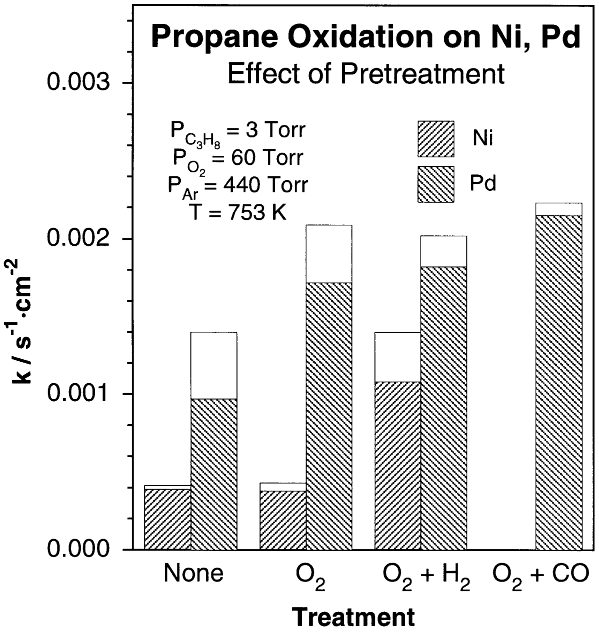

Figure 8. Determination of k (the reaction rate constants) from isothermal kinetic runs designed to probe the effect of different pretreatments on the performance of palladium and nickel foils for the total oxidation of saturated hydrocarbons. All these experiments were carried out with 3 Torr of propane, 60 Torr of oxygen, and 440 Torr of argon at 753 K. Results from four types of pretreatments are reported here, namely (from left to right), (1) none; the catalyst was used immediately after a quick flash to 1000 K under vacuum; (2) a 5 min pre-exposure to 500 Torr of oxygen at 1000 K; (3) 5 min sequential pre-exposures to 500 Torr of oxygen and hydrogen at 1000 K; and (4) 5 min sequential pre-exposures to 500 Torr of oxygen and carbon monoxide at 1000 K (done for the case of palladium only). The hatched bars represent the lower-limit values of k obtained in each case, while the white bars on top indicate the variations seen over a number of runs and illustrate the stability and reproducibility of the different states of the catalysts. The initially reduced metal foils appear to always perform better, and in the case of palladium reduction with CO yields a more reproducible surface.

from its shiny silvery metallic appearance (Ni) to green-black ($NiO{\cdot}H_2O$), but the activity was low: the measured reaction rate constant was about 4×10^{-4} s^{-1} cm^{-2}. A similar reactivity was seen when the catalyst was pretreated by heating it to 1000 K under 500 Torr oxygen, even though in that case the foil was green-black from the start. After cleaning the sample by heating to 1000 K first under 500 Torr of oxygen and then in 500 Torr of hydrogen, however, the measured average rate constant was about 1.2×10^{-3} s^{-1} cm^{-2}, about three times larger than in the other two cases. This change is easy to understand in view of the fact that the color of the oxygen-pretreated foil changed from green-blue (NiO) back to shiny silvery (Ni) upon hydrogen exposures, proving that the combined pretreatment with oxygen and hydrogen regenerates the metallic Ni surface, and that that phase is the one active for the combustion reactions. Three more observations are relevant to the catalytic behavior of the nickel foil: (1) the metallic Ni surface was seen to evolve slowly into the oxide during all the reaction runs; (2) the reaction rates slowed down with time and deviated significantly from first-order behavior; and (3) the kinetic data obtained here was not as reproducible as in the other cases (notice the size of the white bar over the $O_2 + H_2$-pretreated Ni sample in figure 8). Apparently it is not easy for nickel to retain its metallic state under fuel-lean oxidation conditions.

Finally, the Pt samples were cleaned sequentially with oxygen and hydrogen as is commonly done with supported catalysts [45,54,55], and the foil remained shiny and metallic in all cases. No reproducibility problems were encountered with this metal.

4. Discussion

The data reported here broadens the existing database for alkane total oxidation reactions on noble metal catalysts. To begin with, the results obtained in this study corroborate some of the trends presented in previous publications. In particular, a good correlation was observed between C–H bond energies and reactivities, suggesting that the initial activation of the alkane is the rate-limiting step for the overall combustion process [23]. Indeed, the activation energy for alkane oxidation was seen to decrease with hydrocarbon chain length on the three metals studied here [22,42,48–50]. Chain branching seems to also facilitate alkane activation somewhat (compare the rate constant values for *n*- and isobutane in figure 5, and those of the activation energies in table 1), but this effect is not as dramatic as in the case of chain size [22,48,49,56], and the opposite trend has in fact been reported on occasion [57]. Next, the conversion of methane was also proven to be significantly harder than that of any other hydrocarbon [22,23,58]: light-off temperatures as much as 300 K higher than those of the other alkanes were observed for that molecule in our temperature-programmed oxidation experiments (see for instance the data in figure 6).

New information was derived from this investigation as well. In terms of the changes in oxidation activity induced by changing the metal used as the catalyst, platinum foils proved to be more active than palladium samples for all the alkanes studied here. There is little discussion about the fact that platinum is more effective than palladium in catalyzing the combustion of heavier alkanes [22,42,50,59], but a higher activity has been often reported for the oxidation of methane on palladium [1,20,44,50] unless reducing conditions are used [29,60]. To explain the differences in activity trends between our data and those in previous reports, it is important to remember that the unique behavior of palladium-based catalysts towards methane conversion has been ascribed to the presence of some type of oxide on the surface [20,33,49,50]. Here it was also shown that, while the active phase in the case of platinum was the metal, it is indeed the oxide that promotes oxidation with palladium. However, the actual nature of the active site on the palladium-based catalysts has been debated to a great extent in the literature, because it is believed that there is some synergism between the metal and some form of oxygen-containing surface species in a way that makes both oxidation states indispensable for the activity of the catalyst [31,32,37,38,42,43]. In that regard we point to the fact that the main differences in activity reported here are manifested as variations in pre-exponential factors; the activation energy for methane oxidation was in fact lower on palladium than on platinum. We would argue that these variations in the pre-exponential term are likely to reflect changes in the density of active sites. We propose that the low values of A measured here for Pd (table 2) reflects the need of unique sites which require a particular combination of metal and oxide components [38] present only in low concentrations on the surface of the foil. It is also possible that the high values obtained for platinum reflect the ease with which that metal can be kept in its metallic state.

There is another conclusion that can be derived from the fact that the values of the pre-exponential factors for alkane oxidation reactions measured here are quite low. While transition state theory (and experimental results for other surface decomposition reactions) predict numbers of the order of 10^{17}–10^{20} s^{-1} cm^{-2} [61], the largest pre-exponential factor in table 2 is that of propane on Pt, and that reached a value of only about 5×10^5 s^{-1} cm^{-2}. This difference can be easily explained by remembering that besides a collision frequency term, the A factor as calculated here includes the effect of the sticking probability of the reactant, which is particularly low for alkanes on metals [62–66]. In that respect, our observation provides additional support for the idea of the hydrocarbon activation being the rate-limiting step for the overall oxidation. It is also interesting to notice that, while in the case of palladium the pre-exponential factor decreases pretty much monotonically with increasing alkane chain size, for platinum (and to a lesser extent nickel) this parameter goes through a maximum between ethane and propane. Although we do not have an explanation for this behavior at the present time, it appears to account for the reversing in the order of activity between platinum and palladium when going from methane to heavier hydrocarbons [60].

One final point worth bringing up here is the fact that there is very little work published on the catalytic behavior of nickel-based catalysts for oxidation reactions. NiO has been shown to be one of the most active oxides in the catalysis of alkane oxidation [22,51], but the reaction rates on that substrate are still several orders of magnitude lower than those seen on platinum or palladium under the same conditions [1,59]. We are not aware of any previously published work on the reactivity of metallic nickel for hydrocarbon total combustion. Supported nickel catalysts have been shown to be quite efficient for syngas formation as long as the contact times are kept low [67,68], but no evidence for such a pathway was obtained in our batch-reactor experiments. Instead, it was found here that methane total combustion is significantly faster on nickel than on either palladium or platinum (figures 5 and 7). It needs to be pointed out, however, that we found that metallic nickel is the active phase for this reaction, and that such oxidation state is difficult to maintain under the fuel-lean conditions used in these experiments: a slow-down of the reaction rate beyond that expected from first-order kinetics was seen during each individual kinetic run, and the film was seen to become oxidized over time. Nevertheless, it is somewhat puzzling that no significant differences were observed between the kinetics of oxidation of methane and that of the other alkanes on the nickel foil, as it was seen on the other two metals. We believe that in spite of the potential problems related with maintaining the proper oxidation state of the catalyst during reactions, it is worthwhile looking into nickel-based catalysts as alternatives for the design of alkane emission control systems.

5. Conclusions

Kinetic data were obtained in this investigation for the total oxidation of methane, ethane, propane, *n*-butane, and isobutane on nickel, palladium, and platinum foils under fuel-lean conditions by using a micro-batch recirculating reactor. Clear trends were seen on each metal as a function of the nature of the hydrocarbon, the activity increasing with chain size and to a lesser extent with chain branching. The rate laws were in all cases approximately first and zeroth order with respect to the hydrocarbon and oxygen partial pressures, respectively, but some differences were seen in individual cases, presumably because of the different reaction temperatures used in the pressure-dependence determinations. The reactivity of the three metals towards the oxidation of each of the alkanes studied here was contrasted by performing both temperature-programmed oxidation and isothermal oxidation experiments. The activity for the conversion of all the paraffins other than methane was found to follow the trend Pt > Pd > Ni, but methane oxidation was proven to be faster on the nickel foil. By observing the color of the foils during reactions it was determined that the active catalytic phases in the cases of Pt and Ni are their metallic form, but for Pd it is the oxide instead. Most of the differences in reactivity seen among the metals were ascribed to changes in pre-exponential factors, an indication of changes in the surface density of active sites with changing catalyst.

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