Hydrocarbon combustion at high oxygen coverage on palladium: a model study on Pd(100)

Xing-Cai Guo and Robert J. Madix

Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025, USA

Received 9 November 1995; accepted 14 February 1996

Hydrocarbon combustion on Pd(100) was studied using temperature-programmed reaction spectroscopy (TPRS) at high oxygen coverages up to 1.1 oxygen atom per palladium atom. The hydrocarbons studied included both alkenes (propene, 1-butene, and 1,3-butadiene) and arenes (benzene, toluene, and styrene). Alkanes (pentane and cyclohexane) were also studied, but no reaction was detected. It was found that even at 1.1 O/Pd, efficient combustion reactions occur at 350–650 K for all the alkenes and arenes studied. It appears that higher chemisorption energies of hydrocarbon on the surface (butadiene > butene > propene; styrene > toluene > benzene) lead to lower activation energies and higher combustion yields. As the oxygen coverage increases from 0.25 O/Pd, the activation energies for the combustion reactions increase, and the combustion yields pass through a maximum, presumably due to a blocking effect of O(a) on hydrocarbon adsorption.

Keywords: combustion; propene; butene; butadiene; benzene; toluene; styrene; palladium

1. Introduction

The three-way catalytic converter equipped in automobiles is used to remove carbon monoxide (CO), nitrogen oxides ($NO_x = NO$, NO_2, and N_2O_4), and unburned hydrocarbons (HC) from the exhaust. The active ingredients in the conventional three-way catalyst are platinum (Pt), palladium (Pd), and rhodium (Rh). Due to the high demands and high prices of these precious metals, especially Rh, it has recently been attempted to develop a Rh-free three-way catalyst using only Pd [1]. However, little fundamental knowledge has been obtained from these attempts.

In order to gain basic understanding of the combustion reactions, we have recently conducted a series of investigations on hydrocarbon combustion on a single crystal Pd(100) surface [2,3]. Until now we have reported on reactions at low oxygen coverages. In these studies atomically adsorbed oxygen, O(a), was produced by O_2 exposure at 300 K. The combustion reactions of alkenes [2] and arenes [3] were studied on the well-defined Pd(100)–p(2 × 2)-O phase at a coverage of 0.25 O atom per surface Pd atom (O/Pd). At this coverage four-fold hollow sites and two-fold bridge sites are still accessible for hydrocarbon adsorption. A direct, activated, catalytic combustion route was found at low temperatures (< 400 K), in contrast to the indirect reactions which involve dehydrogenation on O(a)-free sites at higher temperature and subsequent oxidation of C and H atoms.

In this letter we report results for hydrocarbon combustion at high oxygen coverage (up to 1.1 O/Pd), which may better simulate the high O_2 pressure conditions in practice. It has been shown previously that dissociative adsorption of NO_2 produces high atomic oxygen coverage on Pt(111) (up to 0.75 O/Pt) [4–6] and on Pd(111) (up to 2.1 O/Pd) [7]. NO_2 dissociates into NO(a) and O(a) on both surfaces; NO desorption is complete at 400 K on Pt(111) and at 500 K on Pd(111). Therefore, when NO_2 is exposed at these temperatures, only O(a) accumulates on the surface. In this work on Pd(100), NO_2 was exposed at 530 K, and experiments showed little NO adsorption.

Besides the p(2 × 2) structure at 0.25 O/Pd, several other ordered O(a) phases have been observed as the coverage increases: [8] c(2 × 2) at 0.50 O/Pd, p(5 × 5) at 0.68 O/Pd, and $(\sqrt{5} \times \sqrt{5})$R27° at 0.80 O/Pd, as well as several mixed phases in between these coverages. For the p(2 × 2) and c(2 × 2) phases, O(a) atoms occupy the fourfold hollow sites [9–11]. For the higher density phases, p(5 × 5) and $(\sqrt{5} \times \sqrt{5})$R27°, two possible oxygen states have been proposed. Orent and Bader proposed that these structures may be oriented layers of surface oxide (PdO) on the Pd(100) substrate [12], whereas Simmons et al. [8] suggested that at 0.80 O/Pd the top layer Pd atoms reconstruct giving rise to distorted fourfold sites where O(a) atoms reside. The less dense O phases are generally found to be more reactive than the more dense phases toward the oxidation of CO and H_2 [8]. Similarly, one would anticipate that hydrocarbons could be less reactive, since adsorbed O would be expected to block adsorption sites. However, we find that even at 1.1 O/Pd, efficient combustion occurs at 350–650 K for all the hydrocarbons studied.

2. Experimental

Experiments were carried out in an ultrahigh vacuum chamber with a base pressure less than 5×10^{-11} Torr. All temperature-programmed reaction spectroscopic (TPRS) measurements were taken with a UTI mass spectrometer interfaced to a desk top computer which is capable of multiplexing up to 200 masses. A nearly linear heating rate of 4 K/s was used for all the spectra recorded. The Pd(100) crystal was prepared using standard metallographic techniques. The Pd(100) surface was initially cleaned by a combination of Ar ion sputtering (600 eV, 10 μA, 300 K), oxygen treatment (10^{-7} Torr, 1000 K), and annealing (1300 K). The clean Pd(100) surface exhibited temperature-programmed desorption spectra for O_2 and CO in excellent agreement with the literature [13,14]. Gaseous alkenes were used from lecture bottles (Aldrich, 99+%) without further purification. Liquid arenes (Aldrich, 99+%) were purified with freeze–pump–thaw cycles before exposure to the surface. NO_2 (Matheson, 99.5%) was used without further purification.

High atomic oxygen coverage was achieved by exposing NO_2 on Pd(100) at 530 K as mentioned above. The crystal was then cooled to 190 K at which the surface was exposed to hydrocarbon vapor.

3. Results and discussion

3.1. Alkene combustion

In the beginning of the experiments an extensive search was conducted for volatile reaction products during temperature-programmed reactions for each hydrocarbon (HC) on Pd(100) at various O(a) coverages up to 1.1 O/Pd. The reaction products detected are as follows:

$$\mathrm{HC(a)} + \mathrm{O(a)} \xrightarrow[\mathrm{Pd(100)}]{190\text{–}1100\ \mathrm{K}} \mathrm{HC(g)}, \mathrm{H_2O(g)}, \mathrm{H_2(g)}, \mathrm{CO_2(g)}, \mathrm{CO(g)}, \mathrm{O_2(g)}.$$

Carbon was left on the surface when O(a) was insufficient for complete combustion. No partial oxidation products were detected.

The temperature-programmed reaction spectra at 1.1 O/Pd are shown in fig. 1 for (a) propene, (b) butene, and (c) butadiene. As the surface temperature is ramped, parent hydrocarbon molecules desorb in several states in the adsorbed monolayer. Multilayer adsorption occurs below 120 K [2] and is not shown. Propene desorbs at 210, 250, and 310 K; butene desorbs at 210, 270, and 320 K; butadiene desorbs at 210 and 350 K. The highest desorption temperature of the parent peaks provides an indication of the relative *molecular adsorption energies* (with minimal repulsive lateral interactions) on the O(a)-covered Pd(100), i.e.

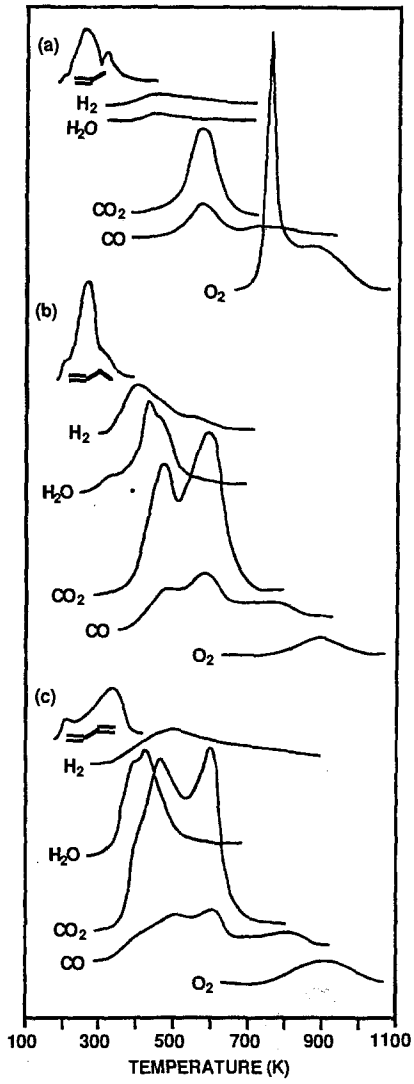

Fig. 1. Temperature-programmed reaction spectra of (a) propene, (b) 1-butene, and (c) 1,3-butadiene on atomic oxygen covered Pd(100) surface at an oxygen coverage of 1.1 O/Pd. Atomic oxygen was adsorbed by NO_2 exposure at 500 K. Alkenes were exposed at 190 K with an exposure of 5 L.

$$\text{propene (18.8 kcal/mol)} < \text{butene (19.4 kcal/mol)} < \text{butadiene (21.3 kcal/mol)},$$

where the energy values are estimated from the peak temperatures, based on the Redhead equation [15] with the assumption of a constant preexponential factor of $10^{13}\ \mathrm{s}^{-1}$ and a constant reaction order of unity.

As the surface temperature increases further, H_2O evolves at 445 K from propene, 440 and 470 K from butene, and 400 and 430 K from butadiene. These temperatures are more than 100 K higher than the H_2O evolution peak temperature from corresponding alkenes on Pd(100)–p(2 × 2)-O (0.25 O/Pd) [2]. The upward temperature shifts indicate an increase in activation energies of the combustion reactions due to the increase in O(a) coverage. Accompanying H_2O evolution, some H_2 desorbs for all three alkenes, possibly the

result of dehydrogenation on the O(a)-free sites created by the reaction. On the clean Pd(100) surface alkene dehydrogenation would occur at a temperature around 300 K.

CO_2 evolves at 590 K from propene, 480 and 600 K from butene, and 410, 470, and 605 K from butadiene. These temperatures are 100–200 K higher than those from Pd(100)–p(2 × 2)-O [2], suggesting again an increased activation energy due to high O(a) coverages. The accompanied CO signals are due to fragmentation of CO_2. CO itself is evolved between about 750–800 K for propene, butene, and butadiene, resulting from O(a) reactions with completely dehydrogenated C(a) [2].

Finally, excess O(a) desorbs associatively from the surface. The peak shape of O_2 desorption from Pd(100) at an initial coverage of 1.1 O/Pd is similar to that shown in fig. 1 (a) except that the low temperature peak is even taller (cf. fig. 2 (b)). For propene less than 0.2 O/Pd was reacted, whereas for butene and butadiene more than 0.8 O/Pd was reacted. The high reactivity at such a high oxygen coverage was unexpected, as O(a) was expected to block the adsorption sites for the alkenes, since at 0.25 O/Pd O(a) totally blocks the combustion reactions of ethylene [16]. Inhibition of the reaction *is* also operative for propene at higher O(a) coverages. As O(a) coverage increases, the combustion yields (H_2O and CO_2) pass through maxima around 0.5 O/Pd (data not shown). However, even 1.1 O/Pd is not sufficiently high to totally block propene combustion. For butene and butadiene, there is no inhibition by O(a) up to 1.1 O/Pd, suggesting that the maximum product yields have not been reached.

The high combustion yields are consistent with low activation energies. Comparing the three alkenes, the lowest H_2O and CO_2 evolution temperatures at 1.1 O/Pd indicate the following order for the activation energies:

(1) for H_2O evolution:

propene (27.3 kcal/mol) > butene (27.0 kcal/mol) > butadiene (24.5 kcal/mol),

(2) for CO_2 evolution:

propene (36.5 kcal/mol) > butene (29.5 kcal/mol) > butadiene (25.1 kcal/mol).

These values were estimated from the peak temperatures based on the Redhead equation [15] with the assumption of a constant preexponential factor of 10^{13} s^{-1} and a constant order of unity. This sequence is probably related to that of molecular adsorption energies obtained above. Stronger binding to the surface may weaken the intramolecular bonds, making them more susceptible to O(a) attack. Furthermore, at such high O(a) coverages binding to the surface may involve some type of direct interactions of the adsorbed hydrocarbon molecules with surface O(a) atoms.

3.2. *Arene combustion*

Fig. 2 displays the temperature-programmed reaction spectra of (a) benzene, (b) toluene, and (c) styrene on Pd(100) at 1.1 O/Pd. As the temperature increases, the same sequence of events occurs as for alkenes. Comparing the highest temperature desorption peak for the three arenes, the molecular desorption peak at the lowest coverage shifts up in temperature from 310 K for benzene, to 370 K for toluene, to 395 K for styrene, indicating a surface-binding energy order:

styrene (24.1 kcal/mol) > toluene (22.6 kcal/mol) > benzene (18.8 kcal/mol).

The same order is seen for the combustion reactivity, as indicated by the lowest peak temperatures for H_2O and

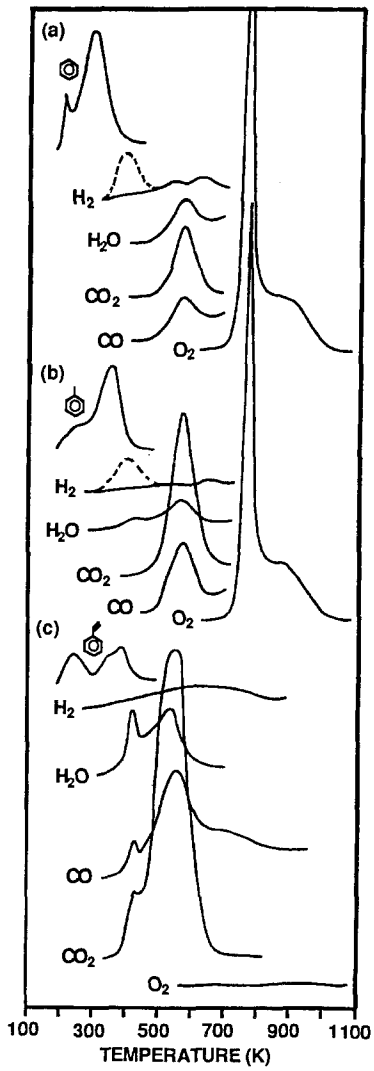

Fig. 2. Temperature-programmed reaction spectra of (a) benzene, (b) toluene, and (c) styrene on atomic oxygen covered Pd(100) surface at an oxygen coverage of 1.1 O/Pd. Atomic oxygen was adsorbed by NO_2 exposure at 500 K. Arenes were exposed at 190 K with an exposure of 5 L. The dashed curves in (a) and (b) are due to H_2 adsorption from the background.

CO_2 evolution. The combustion yields follow the trend as well. The blocking effects due to O(a) are similar for benzene and toluene, but for styrene all O(a) is consumed, again indicating that *O(a) is reactive even at a coverage as high as 1.1 O/Pd.* Compared to those observed on Pd(100)–p(2 × 2)-O [3], the evolution temperatures for CO_2 and H_2O are shifted up, suggesting an increased activation energy due to increased oxygen coverage.

Acknowledgement

The authors gratefully acknowledge the support of the National Science Foundation (NSF CTS-9300188-001) without which this work would not have been completed.

References

[1] T. Sekiba, S. Kimura, H. Yamamoto and A. Okada, Catal. Today 22 (1994) 113.
[2] X.-C. Guo and R.J. Madix, J. Am. Chem. Soc. 117 (1995) 5523.
[3] X.-C. Guo and R.J. Madix, J. Chem. Soc. Faraday Trans. 91 (1995), in press.
[4] J. Segner, W. Vielhaber and G. Ertl, Israel J. Chem. 22 (1982) 375.
[5] M.E. Bartram, R.G. Windham and B.E. Koel, Surf. Sci. 184 (1987) 57.
[6] D.H. Parker, M.E. Bartram and B.E. Koel, Surf. Sci. 217 (1989) 489.
[7] B.A. Banse and B.E. Koel, Surf. Sci. 232 (1990) 275.
[8] G.W. Simmons, Y.-N. Wang, J. Marcos and K. Klier, J. Phys. Chem. 95 (1991) 4522.
[9] K.H. Rieder and W. Stocker, Surf. Sci. 150 (1985) L66.
[10] E.M. Stuve, R.J. Madix and C.R. Brundle, Surf. Sci. 146 (1984) 144.
[11] S.-L. Chang and P.A. Thiel, J. Chem. Phys. 88 (1988) 2071.
[12] T.W. Orent and S.D. Bader, Surf. Sci. 115 (1982) 323.
[13] K. Klier, Y.-N. Wang and G.W. Simmons, J. Phys. Chem. 97 (1993) 633.
[14] R.J. Behm, K. Christmann, G. Ertl and M.A. Van Hove, J. Chem. Phys. 73 (1980) 2984.
[15] P.A. Redhead, Vacuum 12 (1962) 203.
[16] E.M. Stuve and R.J. Madix, J. Phys. Chem. 89 (1985) 105; Surf. Sci. 152/153 (1985) 532.