WORK FUNCTION AND UPS STUDIES OF PROPYLENE AND CYCLOPROPANE ADSORPTION ON PALLADIUM SURFACES

Zdeněk BASTL

J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2

Received January 3rd, 1983

The Kelvin vibrating capacitor method was used to measure the work function changes of vacuum deposited thin palladium layers in propylene adsorption. The work function change found for the propylene-saturated surface is, within the experimental error, identical with the change observed in the adsorption of cyclopropane and equal − 1·085 ± 0·07 eV. Propylene and cyclopropane adsorption leads in the region of higher surface coverages to similar difference UV photoelectron spectra, exhibiting emission bands located at 6·7, 8·2 and 9·3 eV below the Fermi level. It is obvious from the results that at $T \approx 300$ K, the adsorption of propylene and cyclopropane leads at higher coverages with high probability to similar surface complexes.

Palladium catalysts exhibit high catalytic activity and selectivity in the hydrogenation of olefins and other unsaturated hydrocarbons[1]. The present study is aimed to compare the chemisorption of propylene and cyclopropane on clean palladium surfaces. Both mentioned hydrocarbons have the same chemical composition and also their hydrogenation on palladium yields the same product – propane. One can ask whether also the surface complexes formed in the chemisorption of propylene or cyclopropane are similar, or even identical.

In order to solve this problem, we have measured the work function changes of polycrystalline evaporated films caused by the chemisorption of propylene and cyclopropane, as well as, the changes occurring during the hydrogenation of corresponding surface complexes. The results of such measurements cannot solve unequivocally the above mentioned problem but they can contribute to its solution. Results of a study of the work function changes in cyclopropane adsorption on palladium were described in a previous paper[2]. In the present communication, we have studied the adsorption and hydrogenation of propylene and the results are compared with the data obtained for the cyclopropane–palladium system. In an effort to get more information on the structure of the stable surface complexes we have applied in our study also a method of ultraviolet photoelectron spectroscopy (UPS). It should be mentioned that the results obtained by this technique do not always lead to unambiguous identification of the molecular surface complex, particularly in the case of polycrystalline surfaces where usually broad and unresolved bands appear in the spectra.

Let us note that even in the best case of successful identification of the surface complex, one cannot be sure that these complexes represent true intermediates of a catalytic reaction. Taking into account the dynamic character of this reaction, it is not very probable that the intermediates have always a well defined molecular structure.

EXPERIMENTAL

All measurements were performed on polycrystalline thin layers prepared by vacuum deposition of palladium in situ at residual gas pressure $\sim 10^{-7}$ Pa, with the support kept at ~ 300 K. The work function changes caused by the adsorption were measured at room temperature by means of the Kelvin vibrating capacitor method. The experimental arrangement and measurement procedures were described in more detail in previous papers[2,3].

UPS studies were carried out in the ESCA 3Mk II (VG Scientific Ltd., UK) electron spectrometer. Initial cleanliness of the used palladium surfaces was checked by X-ray photoelectron spectroscopy (XPS). The angle between the collected electrons and a normal to the surface of the sample was kept constant, equal 45°. The electron distribution curves were measured using unpolarised He I ($h_\nu = 21{\cdot}2$ eV) radiation. For clean surfaces, the spectra were also recorded with the He II ($h_\nu = 40{\cdot}8$ eV) and X-ray AlK$_\alpha$ ($h_\nu = 1\,486{\cdot}6$ eV) lines. The energy analyzer was operated in the FAT mode, with a 2% resolution determined from broadening of the Fermi edge of palladium. In each case, the spectra were accumulated in a multichannel analyzer for 10 minutes. The emission induced by the presence of the adsorbate as well as selective attenuation of the substrate emission are presented in the form of the difference spectra. These are obtained by subtracting the spectrum of clean surface from that of the surface with the adsorbate. Propylene used in the experiments (Fluka AG, Switzerland, A grade purity) was purified similarly as cyclopropane (ICI Ltd., Great Britain, medicinal purity), by vacuum distillation.

RESULTS AND DISCUSSION

Adsorption of the hydrocarbons was carried out with a series of individual doses. Adsorption of the first several doses proceeded readily and did not yield measurable amounts of products in the gas phase. In this region, the work function slightly increased with each of the doses. After certain surface coverage was reached, any additional dose led to an instantaneous drop of work function value, followed by gradual increase until a stationary value was achieved. The pressure in the gas phase increased in this adsorption region proportionally to the number of the added propylene doses. Additional doses of propylene led only to a decrease of the work function value and increase of the gas phase pressure. The work function changes observed during adsorption of the propylene doses thus resemble changes found in the adsorption of ethylene[4] and cyclopropane[2] on palladium. In all these cases, three regions were observed differing in the character of time-dependence of the work function changes. The dependence of the work function changes on relative surface coverage is shown in Fig. 1. Surface coverage Q is defined as $Q = Q_a/Q^*$, where Q_a denotes the amount adsorbed and Q^* is the adsorbed amount corresponding to the stationary gas phase pressure 3 . 10^{-3} Pa (*i.e.* the lowest pressure which can be detected with the applied thermal conductivity gauge). The maximum drop of work function value, corresponding to surface saturation at a pressure of the gas phase 2 Pa was equal $\Delta\phi = -1{\cdot}085 \pm 0{\cdot}074$ eV. Saturation values of the work function are compared in Table I for the adsorption of propylene, cyclopropane and ethylene on palladium, molybdenum and nickel surfaces. It is evident from these results that, within experimental error, the saturation values of the work function for propylene and cyclopropane adsorbed on palladium are equal. As soon as full surface coverage was reached, the gas phase was pumped out which led only to a slight increase of the work function value, 35 meV. This shows that only a small fraction of the adsorbed species is bound weakly to the surface, or, that the desorbing particles have little effect on the work function value.

After the gas phase was pumped out, hydrogen was introduced to the palladium surface and its reaction with surface complexes of the adsorbed propylene was studied. The work function value, at the end of the hydrogenation reaction, was only by 75 ± ± 10 meV higher than that one of the clean palladium surface. This result seems to indicate that practically all hydrocarbon complexes can be removed from the surface by hydrogenation at room temperature.

The obtained results demonstrate that the adsorption of propylene and cyclopropane lead both, to complexes affecting the work function in a same way. An exception is found for the first stages of the adsorption on a clean surface. The difference observed in the character of the dependence of work function change on surface coverage (Fig. 1) can be, for this region, explained by a more extensive partial dehydrogenation of propylene in adsorption. The time-dependence studies of the work function changes have also indicated that the adsorption rate is in this region higher with propylene than with cyclopropane.

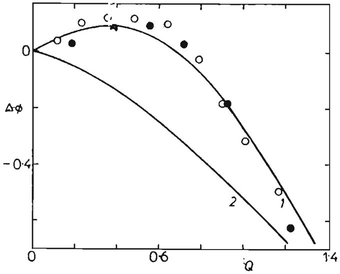

FIG. 1

Dependence of the work function of palladium films $\Delta\phi$ (eV), on surface coverage Q, in the region $0 < Q < 1{\cdot}2$. Curve *1*: adsorption of propylene; curve 2: adsorption of cyclopropane; quantity Q is defined in the text; $T \approx 300$ K. The presented results were obtained with two different films. The curves were drawn through the experimental data using expression $\Delta\phi = -aQ - bQ^2$ (for propylene: $a = -0{\cdot}54$, $b = 0{\cdot}78$; for cyclopropane: $a = 0{\cdot}18$, $b = 0{\cdot}38$)

UPS Results

The clean surface spectra are in agreement with the published data[5-7] (Fig. 2). The correspondence between the calculated densities of electronic states[8,9] and the experimental electron distribution curves is satisfactory.

Eastman[10] brought attention to the photoemission band located 7·5 eV below the Fermi level, which he assigned to surface plasmon excitation. Probability of excitation of these plasmons is usually increased by the surface contamination or by the presence of chemisorbed species. The difference spectra in such cases can exhibit enhanced emission in this energy region which could be misinterpreted for emission from the levels of the surface molecular complex.

Adsorption of propylene at low temperature (~ 100 K) leads to a difference spectrum (Fig. 3, curve 2) which closely resembles spectrum of gaseous propylene (Fig. 3, curve *1*) shifted towards the lower values of binding energies (ionization potentials) by 5.2 eV. The magnitude of this shift is equal to the sum of the work function of the

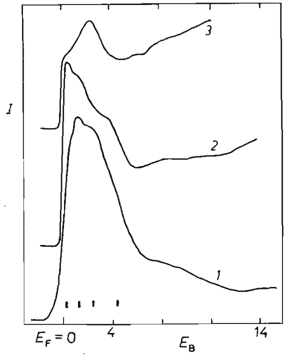

FIG. 2

Photoelectron spectra of the valence band of clean palladium surface. Curve *1*: Al K_α line used for excitation; curve 2: He II spectrum; curve 3: He I spectrum. Bars show the positions of the density of state peaks for palladium. E_B (eV) is the binding energy measured from the Fermi level; *I* is the intensity in arbitrary units

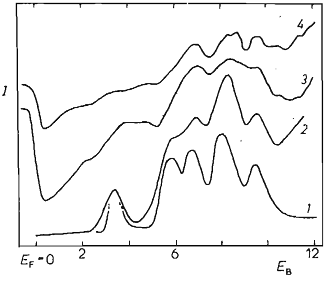

FIG. 3

Photoelectron difference spectra of palladium surfaces after their exposure to 100 L of propylene at $T \approx 100$ K (curve 2), 50 L of propylene at $T \approx 300$ K (curve 3) and 100 L of cyclopropane at $T \approx 300$ K (curve 4; $\Delta\phi = -0.8$ eV). Curve *1* represents a shifted gas phase photoelectron spectrum of propylene (1 L = $1.33 \cdot 10^{-4}$ Pa.s) surface with adsorbed propylene and the relaxation energy. The spectrum corresponds to emission of electrons from the propylene molecules bound weakly (condensed) on a layer of chemisorbed molecules. As one can see from the spectra, this propylene is adsorbed without dissociation of the C–C or C–H bonds.

Adsorption of propylene at room temperature leads to photoemission bands which are centered approximately at 6·7, 8·2 and 9·3 eV below the Fermi level (Fig. 3 curve *3*). Position of these bands agrees well with the values observed[11] for the propylene chemisorbed on platinum (100) single crystal surfaces. It is interesting that the adsorption of cyclopropane on palladium leads nearly to the same ionization features (Fig. 3, curve *4*) as the adsorption of propylene. From this result it may be concluded that at given exposures, similar surface complexes are present on the surface.

The obtained experimental data do not allow to identify unambiguously the molecular structure of the surface complexes. From the similarity of the spectra shown in Fig. 3 one can postulate that the structure of the surface species is not very different from that of the propylene molecule. It is quite probable that the discussed complex has a structure of propylidyne type which is described in literature[14] as forming a stable complex in the adsorption of ethylene on platinum (111) surfaces. One cannot also exclude a presence of propylene complexes bonded to the surface by π–d interaction. In order to remove the ambiguity in assignment of the UPS spectra of surface complexes, one would have to study systematically the spectra of organometallic complexes of palladium with the alkanes.

The adsorption of the studied hydrocarbons results in considerable attenuation of emission from the d-band of palladium, especially from the states which are located just below the Fermi level. This reduction of emission can be accounted to: *1*) The existence of localized electron surface states which are strongly influenced by chemisorption. *2*) Formation of a new level due to the back-bonding effect (for π–d bond

TABLE I

Work function changes achieved at surface saturation, for the adsorption of propylene, cyclopropane and ethylene on palladium, molybdenum and nickel surfaces at $T \approx 300$ K

Gas	Pd	Mo	Ni
C_3H_6	$-1{\cdot}085 \pm 0{\cdot}07$	$-0{\cdot}08 \pm 0{\cdot}07^a$	—
c-C_3H_6	$-0{\cdot}98 \pm 0{\cdot}10^b$	$-0{\cdot}10 \pm 0{\cdot}02^c$	$-0{\cdot}62 \pm 0{\cdot}1^a$
C_2H_4	$-1{\cdot}5^d$	—	$-0{\cdot}42^d$

Experimental data taken from: [a] ref.[13], [b] ref.[2], [c] ref.[3], [d] ref.[4].

of the adsorbed propylene) which has lower photoionization cross-section in comparison with the palladium *d*-states. *3*) Inelastic losses – the emission of inelastically scattered electrons is enhanced by the presence of the adsorbate. Inelastic losses result also in broadening of the photoemission bands and, in this way, also in partial supression of the electron distribution curve structure.

On the basis of the obtained results, it is possible to conclude that at room temperature and at higher surface coverages, propylene and cyclopropane very probably form on palladium surfaces similar surface complexes. Comparison of the obtained results with the results of analogical measurements carried out on molybdenum and nickel surfaces[3,12,13] supports our earlier suggestion concerning the relation between the work function of the given metal surface and its ability to dissociate intramolecular bonds of the adsorbing hydrocarbon molecules. In accordance with this concept we can see, in Table I, that the most extensive fragmentation (the lowest decrease in work function value) is found in the adsorption of propylene or cyclopropane, on molybdenum, which has the lowest work function value from all the listed metals. The relatively large decrease of work function observed in the adsorption on palladium fits well with the high work function value of this metal and, consequently, with the low splitting efficiency of this metal towards C–H bonds of the hydrocarbons during the adsorption.

The author wishes to express his gratitude to Dr Z. Knor for reading carefully this manuscript and for his valuable comments.

REFERENCES

1. Maitlis P. M.: *The Organic Chemistry of Palladium*, Vol. II. Acad. Press, London and New York 1971.
2. Bastl Z.: This Journal *43*, 1943 (1978).
3. Bastl Z.: This Journal *43*, 1665 (1978).
4. Duś R., Lisowski W.: Surface Sci. *85*, 183 (1979).
5. Hüfner S., Wertheim G. K., Buchanan D. N. E.: Solid State Commun. *14*, 1173 (1974).
6. Janak J. P., Eastman D. E., Wiliams A. P.: Solid State Commun. *8*, 271 (1970).
7. Conrad H., Ertl G., Küpers J., Latta E. E.: Discuss. Faraday Soc. *58*, 116 (1974).
8. Moruzzi V. L., Janak J. P., Wiliams A. P.: *Calculated Electronic Properties of Metals*, p. 144. Pergamon Press, London 1977.
9. Louie S. G.: Phys. Rev. Lett. *42*, 476 (1979).
10. Eastman D. E., Cashion J. K., Swittendick A. C.: Phys. Rev. Lett. *27*, 35 (1971).
11. Clarke T. A., Gay I. D., Law B., Mason R.: Discuss. Faraday Soc. *60*, 119 (1975).
12. Bastl Z., Mikušík P.: Atomki Bull. *22*, 31 (1980).
13. Bastl Z.: Unpublished results.
14. Koestner R. J., Frost J. C., Stair P. C., van Hove M. A., Somorjai G. A.: Surface Sci. *116*, 85 (1982).

Translated by Z. Dolejšek.