

# The effect of iodine on the reactivity of H<sub>2</sub>CO formed in CH<sub>2</sub> oxidation on Pd(1 0 0)

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## Abstract

The formation of H<sub>2</sub>CO in the partial oxidation reaction of CH<sub>2</sub> species and the adsorption of H<sub>2</sub>CO on clean and iodine covered Pd(1 0 0) were investigated by means of temperature-programmed desorption (TPD) and photoelectron spectroscopy (UPS). Adsorbed CH<sub>2</sub> was produced by thermal dissociation of CH<sub>2</sub>I<sub>2</sub>. Besides the stabilization of parent molecules by coadsorbed oxygen, the CH<sub>2</sub> fragments selectively oxidized by preadsorbed oxygen to H<sub>2</sub>CO in a reaction-limited process. The amount of formaldehyde saturates at  $\theta_{\text{O}} = 0.2$ , while the total oxidation products (CO<sub>2</sub>, H<sub>2</sub>O) monotonously increased with the increase of  $\theta_{\text{O}}$ . In separate experiments the surface chemistry of H<sub>2</sub>CO was investigated on clean and iodine covered surfaces. The decomposition of H<sub>2</sub>CO was blocked by preadsorbed I. These feature is interpreted by site blocking, by weakening of the H<sub>2</sub>CO-Pd bond and by decreasing the bond energy between Pd and O by 50 KJ/mol. The results suggest that the electronegative additives promote the selective oxidation of CH<sub>2</sub> species on Pd(1 0 0) surface.

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## 1. Introduction

The coupling and reactions of hydrocarbon fragments (CH<sub>2</sub>, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, etc.) with adsorbed oxygen atoms represent important elementary steps in the selective and total oxidation of hydrocarbons and also in the reforming of methane to produce synthesis gas [1,2]. Previous works showed that CH<sub>2</sub> produced by the thermal and

photo dissociation of adsorbed CH<sub>2</sub>I<sub>2</sub> on metal surfaces [3,4] and readily reacts with adsorbed oxygen atoms to give H<sub>2</sub>CO, which is desorbed immediately after its formation [5]. The surface chemistry of CH<sub>2</sub> was widely studied in our research group earlier on clean and oxygen covered Pd(1 0 0). In the case of a clean surface, the CH<sub>2</sub> species underwent dehydrogenation and hydrogenation processes producing CH<sub>4</sub>, while a small fraction recombined to form C<sub>2</sub>H<sub>4</sub> at 160–230 K [6]. Preadsorbed oxygen atoms reacted with CH<sub>2</sub> above 150 K producing H<sub>2</sub>CO in a reaction limited process [7]. Above 200 K, the oxidation of methylene moieties led to the formation of

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unstable surface complexes. In harmony with theoretical considerations, the presence of HCOO intermediate was confirmed by UPS [7]. The thermal treatment of this layer produces adsorbed OH and CO being further oxidized to H<sub>2</sub>O and CO<sub>2</sub> above 370 K. Similar surface intermediates were established in the oxidation of aldehyde by HREELS on Pd(1 1 1) [8].

We mention that halogen containing compounds, especially iodo-C<sub>1</sub> hydrocarbons are of technological importance [9]. As the additives promotes the selective oxidation pathway. The most promising catalysts seemed to be silver catalysts due to their unique catalytic properties in ethylene oxidation and methanol selective oxidation to formaldehyde [10,11]. An other candidate is copper [12]. In contrary, on Pd(1 0 0)-p(2 × 2)-O surface the total combustion of alkenes could only be observed [13].

As a continuation of our previous work, in the present study we focus on the partial oxidation processes on Pd(100) surface. We analyze the formation of formaldehyde and the total oxidation products as a function of surface oxygen coverage. In order to understand the nature of the partial oxidation process, in separate experiments we investigated the stability of H<sub>2</sub>CO on clean and iodine covered Pd(100).

## 2. Experimental

Experiments were carried out in an ultrahigh vacuum chamber with a base pressure of  $4 \times 10^{-10}$  mbar, equipped with facilities for Auger electron spectroscopy (AES) and ultraviolet photoelectron spectroscopy (UPS) and temperature-programmed desorption spectroscopy (TPD). The electrons were detected by an electrostatic hemispherical electron analyzer (Leybold–Heraeus LHS 10). Collection time for UPS was 15 min. Sample cleaning was achieved by both argon ion sputtering and cycles of oxygen treatments ( $3 \times 10^{-7}$  mbar local pressure, for 10–30 min at the sample temperature of 800–1200 K). No oxygen, sulphur, phosphorus and carbon impurities were detected by AES. The heating rate for TPD measurements was  $7.0 \text{ K s}^{-1}$  from 90 K to the selected tempera-

ture. Gases were dosed through a capillary of 0.1 mm diameter, which terminated 2 cm from the sample. The pressure around the sample was about  $10^{-7}$  Pa during dosing. CH<sub>2</sub>I<sub>2</sub> and H<sub>2</sub>CO were obtained from Fluka and were further purified by several freeze-pump-thaw cycles. The adsorption of oxygen was performed at 300 K, while adsorption of CH<sub>2</sub>I<sub>2</sub> and H<sub>2</sub>CO was performed at 90 K. According to the previous measurements, the surface concentration of oxygen on Pd(100) (based on TPD experiments) at saturation is  $6.6 \times 10^{14}$  O atoms cm<sup>-2</sup> [14]. This value is considered to be  $\theta_{\text{O}} = 0.5$ , it was confirmed in our case by the occurrence of the narrow  $\gamma$  state in the O<sub>2</sub>-TDS. The iodine layer was prepared by the adsorption of desired amount of CH<sub>2</sub>I<sub>2</sub> at 100 K and subsequent annealing at 600 K. The relative concentration of iodine was followed by TPD and AES. The saturation concentration of I was assumed to be  $\Theta_{\text{I}} = 0.5$  [6,15].

## 3. Results and discussion

### 3.1. Formaldehyde adsorption on clean and iodine-covered Pd(100) surfaces

In accord with the experiments of Scott and Madix [16] and our previous results [17] the formaldehyde is very unstable on clean Pd(100) surface. The weakly held (condensed) H<sub>2</sub>CO desorbed with  $T_{\text{p}} = 120$  K. Another fraction readily decomposes to CO and H<sub>2</sub>. TPD spectra are shown on Fig. 1. The coadsorbed iodine altered the surface chemistry of formaldehyde. Two important and surprising observations can be seen on the thermal desorption spectra (Fig. 1): (i) the amount of desorbed H<sub>2</sub>CO has been intensified and new states of molecular H<sub>2</sub>CO desorption developed between 200 and 300 K, and (ii) no decomposition products (CO and H<sub>2</sub>) were observed in the presence of I<sub>(a)</sub>.

From iodine covered surface the desorption of the parent molecule was only detected. The two low temperature states at 120 and 155 K can be assigned to physisorbed and/or condensed states. In addition, two broad high temperature peaks can be distinguished with  $T_{\text{p}} = 220\text{--}235$  and  $268\text{--}280$  K.

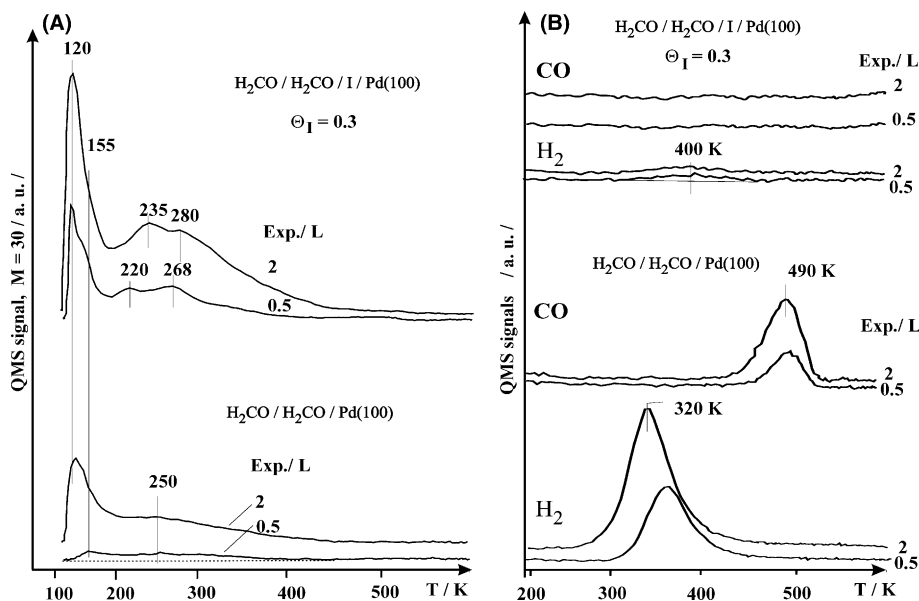


Fig. 1. Thermal desorption spectra for formaldehyde (A) and its main decomposition products CO and H<sub>2</sub> (B) from clean and iodine covered Pd(100) at two different H<sub>2</sub>CO exposures, 0.5 and 2 L, respectively.

Taking into account the desorption activation energy for this state (48–55 kJ/mol) it is possibly due to chemisorbed layer. The absence of decomposition products rules out the existence of  $\eta_2$ -H<sub>2</sub>CO (side-on) beyond 250 K, which would be the reactive surface species [8].

UPS experiments revealed that on clean Pd(100) the formaldehyde adsorption produces two strong emissions at 10.8 and 8.1 eV which can be attributed mostly to the molecular orbitals of adsorbed CO (Fig. 2). A weak photoemission at 13.7 eV may indicate the presence of small portion of weakly held H<sub>2</sub>CO. This latter feature disappeared when the surface was heated to 140 K. In the presence of iodine the intensity of the adsorbate induced spectral features decreased. After smoothing and subtracting of the spectrum of clean Pd(100) from the spectra taken on iodine covered surface, photoemissions appeared at 5.1, 8.4, 9.9, 11.8, 13.6, and 14.8 eV. These peaks are characteristics for the presence of weakly held H<sub>2</sub>CO, which was observed on Ru [18] and Cu [19]. (The adsorbed iodine contributes to the peak at 5.1 eV.) The structure of the spectra remained practically the same at 150 K. The most important change is

the intensification of the peak at 11.5 eV. This observation could be connected with an electron donation from the metal to the 2A<sub>1</sub> molecular orbital of H<sub>2</sub>CO or more probably this changes are due to reorientation of the molecule. We are inclined to think that formaldehyde is in a single bonded  $\eta_1$ -H<sub>2</sub>CO (end-on) state on this surface, which was observed on O-covered Pd(111), too [8]. Further heating to 300 K the photoemission peaks completely diminished, except iodine photoemission at around 5.1 eV.

The structure of the iodine layer at  $\Theta_I = 0.3$ , falls between the p(2×2) and c(2×2). A schematic interpretation for H<sub>2</sub>CO adsorption on I/Pd(100) surface can be seen in Fig. 4. Only a limited number of surface Pd atoms can be iodine free. On these iodine free sites the formaldehyde molecule may bound with its O-end.

### 3.2. Surface reactions in the CH<sub>2</sub>I<sub>2</sub> + O coadsorbed layer

The surface reaction between CH<sub>2</sub>I<sub>2</sub> and oxygen leads to the formation of new products, CO, CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>CO. Due to preadsorbed oxygen the

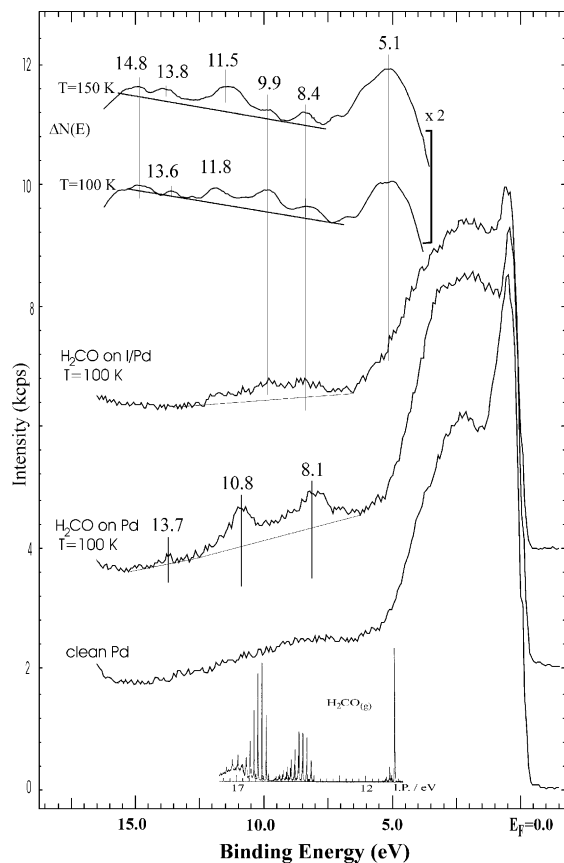


Fig. 2. He II UPS spectra of clean Pd(100), H<sub>2</sub>CO adsorbed on clean Pd(100) and on I/Pd(100) at  $\Theta_{\text{O}} = 0.3$  at 100 K and at 150 K. In both cases the exposures were 2 L. The gas-phase spectrum of H<sub>2</sub>CO from [18].

formation of C<sub>2</sub>H<sub>4</sub> diminished and the amount of CH<sub>4</sub> decreased by a factor of 2 at  $\Theta_{\text{O}} = 0.5$  compared to the clean surface. The measured TDS peak areas for the products of partial and total oxidation were plotted in the function of  $\Theta_{\text{O}}$  in Fig. 3. The figure shows that the amount of formaldehyde saturates at  $\Theta_{\text{O}} = 0.2$ , while the total oxidation products monotonously increased with the oxygen coverage (Fig. 3A).

It would be highly important to check the consumption of oxygen during the surface reactions. Unfortunately, the precise determination of oxygen signal by AES, UPS, XPS in coadsorbed layer is not possible due to the overlappings. TPD gives the only chance to follow the changes in surface oxygen (Fig. 3B). O<sub>2</sub> desorbed in high

temperature peak ( $T_{\text{p}} = 820$  K) from Pd(100) at  $\Theta_{\text{O}} = 0.5$ . (At this high oxygen coverage a peak with small intensity due to physisorbed state appeared at 140 K.) When oxygen coverage,  $\Theta_{\text{O}}$  was only 0.05, a small O<sub>2</sub> desorption was detected at  $T_{\text{p}} = 860$  K. (This shift represents a usual second order kinetics.) The adsorption of 1 L CH<sub>2</sub>I<sub>2</sub> on Pd(100) with precovered oxygen at  $\Theta_{\text{O}} = 0.5$  dramatically changed the TPD curve of O<sub>2</sub>: the low temperature peak significantly intensified, and shifted upward to 180 K. In contrast, the high temperature peak shifted downward to 620 K and became much smaller. This indicates the consumption of surface oxygen in the surface reaction. The total amount of desorbed oxygen at this low CH<sub>2</sub>I<sub>2</sub> exposure was less by 60% compared to the clean surface. (At higher exposures the consumption of oxygen is increased.) The downward shift of the high temperature O<sub>2</sub> peak (presumably due to I<sub>(a)</sub> formed in the dissociation of CH<sub>2</sub>I<sub>2</sub>), points to the decrease in O<sub>2</sub> desorption activation energy. Assuming a pseudo first order kinetic and a pre-exponential factor of 10<sup>13</sup> s<sup>-1</sup>—this decrease is about 50 KJ/mol.

### 3.3. Interpretation of the interaction between CH<sub>2</sub>I<sub>2</sub> and O–Pd(100) surface

We may speculate on the mechanism of the interaction of adsorbed CH<sub>2</sub>I<sub>2</sub> with adsorbed O on Pd surface. Before the adsorption of CH<sub>2</sub>I<sub>2</sub> we produced a chemisorbed oxygen layer with a nominal coverage of 0.5. According to the literature [14,20] at this O coverage patches of p(5×5) and ( $\sqrt{5} \times \sqrt{5}$ )R27° are formed. Due to the relatively low surface concentration of O-free Pd the incoming CH<sub>2</sub>I<sub>2</sub> molecules might stick transiently on the O-covered surface. This metastable structure start to accommodate with an insertion of the I-end of the molecules at the “more open” sites among the imperfect parts. A schematic drawing in Fig. 4 is to help in understanding. The length of the C–I bond increases and the bond finally breaks [7]. The driving force of the dissociation is the formation of strong Pd–I bond. On the other hand, the oxygen atom is pushed away from the surface and forced to react with CH<sub>2</sub>. The reaction between O and CH<sub>2</sub> starts at around 180 K, pro-

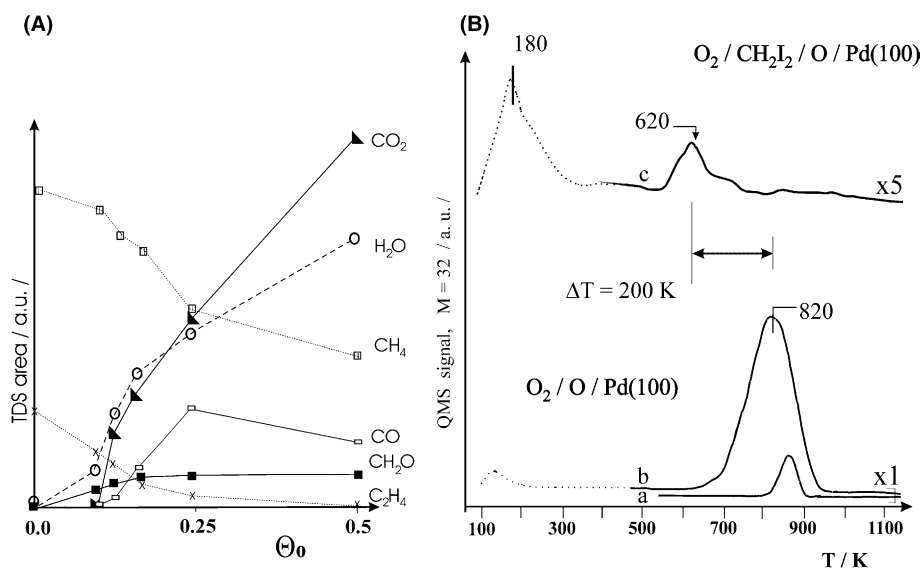


Fig. 3. (A) The amounts of the products for total and  $\text{H}_2\text{CO}$  partial oxidation of  $\text{CH}_2\text{I}_2$  versus initial oxygen coverage at 1 L  $\text{CH}_2\text{I}_2$  exposure. (B) Oxygen thermal desorption spectra from Pd(100) at  $\Theta_O = 0.05$  (a) at  $\Theta_O = 0.5$  (b), and (c)  $\text{O}_2$  TPD from  $\text{CH}_2\text{I}_2/\text{O-Pd}(100)$  ( $\Theta_O = 0.5$ ).

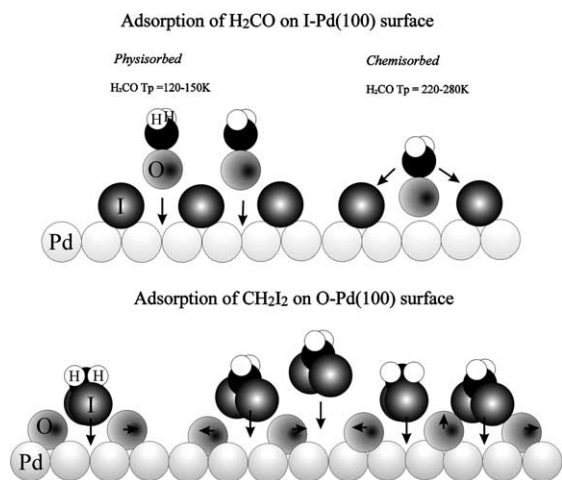


Fig. 4. Schematic interpretation of surface structure of  $\text{H}_2\text{CO} + \text{I}$  layer on Pd(100) (upper part). The “metastable layer”, coadsorption of  $\text{CH}_2\text{I}_2$  and O atoms on Pd(100) (lower part).

ducing partial oxidation product ( $\text{H}_2\text{CO}$ ). A few O may also recombine resulting in the increase of the low temperature desorption of  $\text{O}_2$  at  $T_p = 180$  K. Those reaction intermediates, which are shadowed by I atoms cannot further react with oxygen and/or thermally decompose.

When chemisorbed oxygen is reacting with small  $\text{CH}_2\text{I}_2$  exposures, the  $\text{O}_2$  desorption peak (which show second order kinetics [14,20]) is shifted to lower temperature. When interpreting this unusual finding, an electrostatic effect of the adsorbed iodine has to be considered, because the site blocking effect alone would have an opposite effect on this second order reaction [20].

#### 4. Conclusions

- (1) Preadsorbed iodine stabilizes  $\eta_1\text{-H}_2\text{CO}$  adsorbed species and prohibits its further decomposition.
- (2)  $\text{CH}_2$  is mainly partially oxidized up to  $\Theta_O = 0.2$ , beyond this oxygen coverage the total oxidation of  $\text{CH}_{2(a)}$  is the main reaction.
- (3) Surface iodine has a site blocking effect on the incoming coadsorbates.

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