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# RESEARCH ON CATALYSIS BY MEANS OF RADIOCHLORINE $Cl^{36}$

## Part II. State of Chlorine Deposited on Catalysts

By

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### Introduction

It was found as reported in Part I<sup>(1)</sup> that chlorine actually deposits on all test pieces when treated by radioactive  $HCl^*$ . The present paper is concerned with further investigations of the state of deposition on these catalysts.

#### § 1. Test Piece of Zinc.

Zinc test piece which acquired the largest radioactivity and change in appearance by the  $HCl^*$  treatment as shown in Table I of Part I was soaked in 20 cc distilled water at room temperature for 24 hours, washed, dried and its radioactivity determined similarly as in § 3 of Part I at 38 ct/min inclusive of background count as shown in the third column of Table I. The small excess over the background count given by the figure in the parenthesis was completely lost by further soaking as shown in the last column of Table I. Zinc ion in the water used for soaking was qualitatively detected by white precipitate formed by bubbling hydrogen sulfide through the water preliminarily added with ammonia on one hand and its chlorine ion content determined at 0.5 mg by MOHR's method on the other hand. The latter quantity of chlorine ion was in concordance with 0.46 mg chlorine deposition as calculated from the loss  $584 - 34 = 550$  ct/min of count by soaking and the specific radioactivity 1200 ct/min.mg  $Cl$  of the sample as found in § 4 of Part I.

It is concluded from these results that macroscopic phase of zinc chloride was formed on the test piece by the  $HCl^*$  treatment.

(1) J. HORIUTI, K. TANABE and Y. WATANABE, This Journal.

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TABLE I.

Radioactivities after Soaking of Test Pieces Treated by  $HCl^*$ .

Test pieces	Count before soaking ct/min.	Count after the 1st soaking ct/min.	Count after the 2nd soaking ct/min.
<i>Zn</i>	584	38 ( 4)	33 (0)
<i>Fe<sub>3</sub>O<sub>4</sub></i>	275	48 (14)	34 (0)
<i>Fe</i>	139	30 ( 0)	—
<i>Ni</i>	141	41 ( 7)	33 (0)
<i>Au</i>	62	30 ( 0)	—
<i>Cu</i>	56	30 ( 0)	—
<i>Graphite</i>	134	40 (10)	35 (1)
<i>Ag</i>	55	33 ( 0)	—
<i>Pt-Pt</i>	152	150	—
<i>Pd</i> (1)*)	57	34 ( 0)	—
<i>Pd</i> (4)*)	47	34 ( 0)	—

\*) *Pd* (1) and (4) respectively those of Table I and IV of Part I.

### § 2. Test Piece of Platinum.

As shown in Table I of Part I, bright platinum neither acquires radioactivity nor changes appearance by the treatment in contrast with zinc. The bright platinum being inadequate for the purpose of investigating the deposited state because of its immeasurably small radioactivity, *Pt-Pt* was used in its place.

Treated *Pt-Pt* was soaked in about 10 cc distilled water, washed, dried and its radioactivity determined as in the case of zinc to find invariably 150 ct/min as before. The water used for soaking which has shown no *pH* change as observed by *pH* test paper was added with about 10 mg non-radioactive *NaCl*, evaporated up to dryness, the resulting *NaCl*\* powder collected and its radioactivity determined by the method of §3 of Part I, no measurable excess over the background count being found in confirmation of the above results.

These facts indicate that chlorine deposited on *Pt-Pt* is not soluble in water in contrast with the case of zinc.

One side of the above *Pt-Pt* plate was now coated with paraffin and the other cathodically polarized with ca. 3 ampere current in 20 cc aqueous solution of 10 mg *NaOH* for 20 minutes against platinum

anode. The *Pt-Pt* plate was dried and its radioactivity determined at 90 ct/min inclusive of background count.

The solution used for the polarization was neutralized with non-radioactive *HCl*, evaporated up to dryness, the radioactivity of the residue determined by the method of §3 of Part I at 88 ct/min inclusive of background count. The excess count of the residue  $88 - 34 = 54$  ct/min is almost coincident with the count loss  $152 - 90 = 62$  ct/min of *Pt-Pt* by polarization.

This indicates that deposited chlorine has gone into the solution by the cathodic polarization and that there are no absorption of radiation by *Pt-Pt* particles on the surface: for, if at all, the count loss of *Pt-Pt* should have been less than the excess of the residue.

The above *Pt-Pt* was now subjected to further cathodic polarization similarly for 60 minutes to find its radioactivity decreased to 70ct/min and then for 120 minutes without any more decrease each with a new portion of solution. There are hence two parts of deposited chlorine, one removable by the cathodic polarization and the other not.

The removable part may adequately be attributed, as did for the whole part in Part I, to the monolayer of chlorine atoms each combined to one surface atom, it being nevertheless insoluble in water in distinction from such one as forming platinum chloride crystal and its count  $152 - 70 = 82$  ct/min smaller than the greatest possible value 1000 ct/min derived from the picture in §5 of Part I.

This picture provides an explanation for the observation of KANEKO that the catalytic activity of *Pt* to the exchange reaction between hydrogen and hydrogen chloride steadily decreases as one repeats the measurement,<sup>(2)</sup> while that between hydrogen and water or hydrogen and ammonia was reproducibly observable,<sup>(3)</sup> provided that chlorine at the state retards the exchange reaction.

The unremovable part might, on the other hand, be provisionally attributed to that diffused inside.

### § 3. Test Pieces of Palladium and Glass.

The *Pd* test piece treated by *HCl*\* under the condition of Table I of Part I was investigated, perior to soaking, by microphotograph of 160 magnification in comparison with untreated one to find numerous

(2) Y. KANEKO, unpublished.

(3) Y. KANEKO, "Catalyst" 6, 8 (1950); 6, 28 (1950); 7 98 (1951).

spots on the former as shown in Fig. 1. The surface of the latter was so homogeneous that the focussing was only possible by streaking it as seen in the photograph. The spots were absent, as observed directly by microscope, immediately after the test piece was taken out from desiccator but appeared within about half an hour required for photographing and disappeared when brought back into desiccator and reappeared reversibly by exposing it to external air.

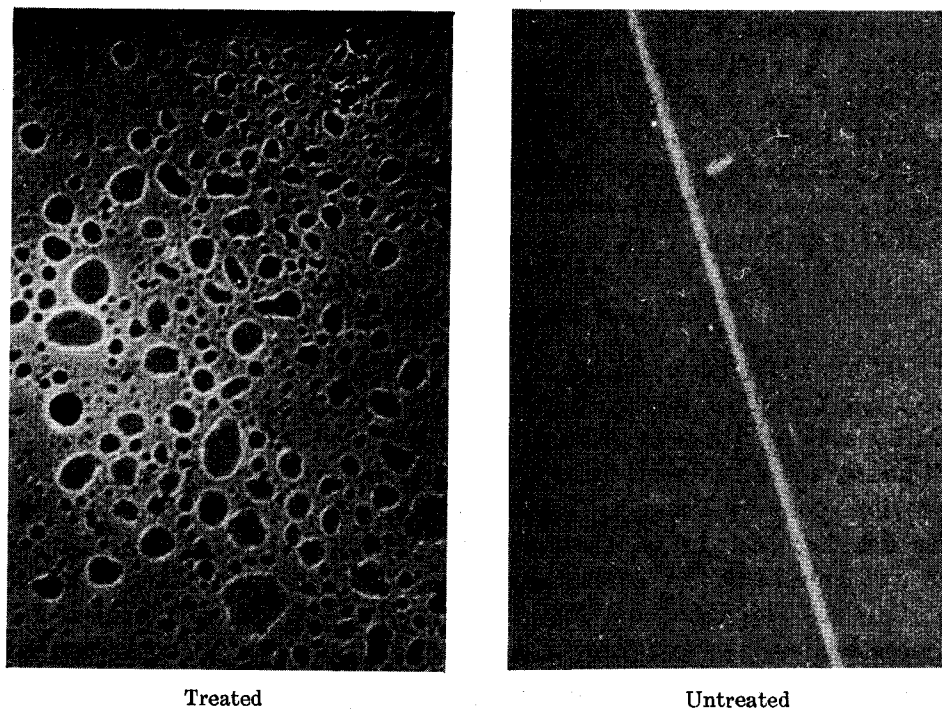


Fig. 1.  
Microphotograph of Palladium Film

Treated *Pd* test pieces of Table I and IV of Part I were now soaked each in 5 cc distilled water at room temperature for 24 hours, washed, dried and their radioactivities determined similarly as in the case of *Zn* to find no excess over the background count both in the cases as shown in Table I.

The waters used for soaking were respectively added with 10 mg non-radioactive *NaCl*, evaporated up to dryness and radioactivities of the residues determined by the method of §3 of Part I at 55 and 47

ct/min inclusive of background count, which are respectively coincident with those of test pieces before soaking.

These results indicate that the deposited chlorine forms stoichiometric palladium chloride, known to be soluble and even deliquescent, being responsible for forming the spots of droplet in moist air.

This does not necessarily conclude the state of chlorine on the *Pd* catalyst prepared by reducing palladium chloride of the selective oxidation<sup>(4)</sup> mentioned in the introduction, since the evaporated film used in the present work might afford the different state to deposited chlorine.\*) Further experiments are required to settle this point.

The state of chlorine deposited on glass\*\*\*) was investigated by soaking similarly as in the above cases to find the imparted radioactivity completely lost as shown in Table I. Sodium ion of the common glass used might have been responsible for the chlorine deposition: similar experiment with silica is of interest in this connection.

#### § 4. Test Pieces of Other Materials.

Other test pieces than those of *Zn*, *Pt* and *Pd* used in experiments of Table I of Part I were now similarly investigated as in the case of *Zn* by soaking them in 20 cc distilled water at room temperature for 24 hours, their radioactivities being determined as given together with previous ones in Table I. In the case of *Ag*, 6*N* ammonia was used for soaking instead of pure water. "Count before soaking" in the second column of the Table was that quoted from the Table I and IV of Part I. The third and fourth column give the radioactivities of test pieces inclusive of background count measured after 24 hours' soaking and that after further 24 hours' soaking respectively, the excess over the background count being given in the parenthesis.

As shown in the Table, the radioactivities of all test pieces except *Pt-Pt* are almost lost by the first soaking and completely by the second one. It is now concluded that chlorine deposited on them forms water soluble (aq. ammonia soluble in the case of *Ag*), stoichiometric chlorides. This conclusion is supported by the liberation of the uncondensed gas by liquid air, perhaps hydrogen, by the *HCl*\* treatment.

Similar conclusion could, however, not be extended straightforward

(4) J. HORIUTI and Y. WATANABE, "Catalyst" 9, 36 (1953).

\*) Cf. the foot-note (\*\*\*) to page 8, Part I.

\*\*) "Glass only" in Table IV of Part I.

*Research on Catalysis by Means of Radiochlorine Cl<sup>36</sup>*

to the case of graphite, since ferric oxide and clay minerals contained as impurities might well be responsible for apparently the same results.

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