RESEARCH ON CATALYSIS BY MEANS
OF RADIOCHLORINE \( Cl^{36} \)

Part I. Treatment with Radioactive Hydrogen Chloride

By

Juro Horiuti, Kozo Tanabe and Yoshihiro Watanabe (*)

Introduction

Two of the present authors found that the catalytic activity of 
\( Pd, Pt, Ni \) and \( Cu \) for the selective oxidation of hydrogen in carbon 
monoxide was markedly promoted by a trace of \( HCl \) in gas, whereas 
that of \( Fe_2O \), not affected at all. (1)

It is the purpose of the present research to investigate the state 
of chlorine deposited, if at all, on these catalysts. Test pieces of these 
catalysts were thus kept, together with those of other materials for 
comparison, at 250°C, the temperature of the selective oxidation, in 
the atmosphere of radioactive hydrogen chloride \( HCl^* \) for 8 hours and 
the chlorine deposition was then detected by means of G-M counter.

Materials (§1), treatment with \( HCl^* \) (§2), radioactivity measurement 
(§3), investigation of quantity-radioactivity relation (§4) and results (§5) 
are described below.

§ 1. Materials.

Radioactive Sodium Chloride \( NaCl^* \).

Radioactive sodium chloride was recovered from the waste solution** of 
aqueous \( HCl^* \) supplied by U. S. Atomic Energy Commission used in 
several previous experiments. (2)

Radioactive chlorine ion was precipitated as \( AgCl^* \) by adding aqueous 
silver nitrate to the waste solution, the precipitate filtered and 
then allowed to stand together with zinc powder and very diluted

*) Visiting Chemist from the Sumitomo Chemical Industry Ltd.
** The solution contains, besides, \( Na^+, SO_4^{2-} \) and decomposition products of \( CHCl_3 \) 
and \( CCl_4 \).
(1) J. Horiuti and Y. Watanabe, "Catalyst" 9, 36 (1963).
(2) J. Horiuti and K. Tanabe, Proc. Japan Acad. 27, 404 (1951); 28, 127 (1952); 28, 
130 (1952).
sulfuric acid for about a week at room temperature to complete the reaction,

\[ 2AgCl^* + Zn \rightarrow 2Ag + Zn^{++} + 2Cl^- \]

The reduced silver and excess zinc powder were filtered off and zinc ion precipitated by adding sodium hydroxide solution, the filtrate being carefully evaporated up over a water-bath to obtain solid NaCl*.

The present procedure was controlled against the loss of Cl* by means of the radioactivity measurement; for instance, zinc hydroxide precipitate was washed with distilled water until the radioactivity of the washings became immeasurable.

The purity of NaCl* thus prepared was 96.0% as determined by Mohr's method.

Radioactive Hydrogen Chloride HCl*.

About 800 mg of NaCl* of the preceding section was cooled by liquid air in glass blind tube T1, which was connected to vacuum line through a normal joint and vacuum cock C1 as shown in Fig. 1, added with 1 cc concentrated sulfuric acid, evacuated to 10⁻⁶ mmHg, then

---

**Fig. 1. Apparatus**

C1~C10: Vacuum Cock,  
T1~T4: Blind Tube,  
M: Manometer,  
Mc: McLeod Gauge,  
Tr: Trap,  
V1: Flask,  
R: Glass Tube,  
Th: Thermocouple,  
S: Glass Frame,  
P: Test Piece,  
N: Copper Gauze,  
H: Electric Furnace,  
Sm: S enlarged,  
Pm: P enlarged,  
VP: Vacuum Pump.
gradually warmed up to 50–60°C, the evolving $HCl^*$ collected in tube $T_1$ cooled by liquid air and having closed $C_1$, $HCl^*$ was further distilled into tube $T_2$ containing phosphorus pentoxide and then back again from $T_2$ to $T_1$: this was repeated several times for drying $HCl^*$, which was finally distilled into tube $T_1$ through $C_2$, $C_3$, $C_4$, the latter then closed, the distillate allowed to evaporate into $V_1$ and stored there.

Test Pieces.

Plates of $Cu$ (0.62), $Zn$ (0.17), $Ag$ (0.08), $Pt$ (0.08) and $Ni$ (0.25) each of $1 \times 2 \text{cm}^2$ size and of the thickness given in the parentheses in mm were polished first with rough emery paper and then gradually with finer ones.

The test piece of $Fe$ (0.30) was prepared from zinc coated iron plate of $1 \times 2 \text{cm}^2$ by removing the coating by aqueous hydrogen chloride and polishing it as above and that of $Fe_3O_4$ by heating the iron plate of the same preparation in air to form black film of $Fe_3O_4$ on it.

The test pieces of $Pd$ and $Au$ were prepared by heating wires of respective materials in vacuum to form evaporated films on $1 \times 2 \text{cm}^2$ glass plates, pure plates being not available at the moment. The amount of $Pd$ or $Au$ of the film was determined at 0.20 or 0.15 mg respectively by weight decrease as removed by aqua regia. Both of them were of the same appearance to that of evaporated aluminum film of 400–500 Å thickness.

The test piece of graphite was prepared by cutting its crystal in $1 \times 2 \times 0.5 \text{cm}^3$ size.

These test pieces were preserved immediately after preparation in a desiccator.

Platinized platinum ($Pt$-$Pt$) was prepared as usual, from two round platinum plate of 2.5 cm diameter and 0.2 mm thickness by electrolyzing 35 cc solution of 1 gm chloroplatinic acid by these plates kept at 1 cm apart with about 0.2 ampere current, commuted every 3 minutes, for half an hour. $Pt$-$Pt$ thus prepared was stored in distilled water.

§ 2. $HCl^*$ Treatment.

Test pieces were treated as shown in Fig. 1 by placing them, mounted on a glass frame, in a glass blind tube $R$ of 180 cc capacity, which was connected to the vacuum line and enclosed in an electric furnace, being wrapped up in copper gauze to ensure the homogeneity
of temperature, which was measured by a thermocouple inserted between R and the gauze. Having kept R thus at 250°C and 10⁻⁶ mmHg vacuum for several hours, HCl⁶ stored in V₁ allowed to expand into R and the pressure read by manometer M. C₁₀ was now closed and R left at the temperature for a recorded time. Tube T₁ was now communicated with R, cooled by liquid air, the pressure of uncondensed gas thus measured by McLeod gauge Mc, the furnace removed, R disconnected from the vacuum line and the radioactivity of test pieces determined by the method described in the next section.

![Diagram of G-M Counter and Pattern of Papers](image)

Fig. 2.

§ 3. Radioactivity Measurement.

The relative position of the sample to the G-M counter at the measurement was fixed by means of glass plate with patterns A and B of papers pasted on one side: the sample was placed on the other side just above B (1 × 2 cm²) and the same side was pressed to the bottom plane of the G-M counter just to fill up the circle left clear by A. In the case of Pt-Pt, B was replaced by a circular pattern of
2.5 cm diameter.

Blank count of the glass plate without sample was taken before and after every radioactivity measurement of the test pieces for control of contamination and it was replaced if at all.

§ 4. Relation between Radioactivity and NaCl* Quantity.

The relation between the radioactivity and NaCl* quantity was investigated as follows for determining the amount of chlorine deposition from the radioactivity measurement.

One to ten mg finely ground powder of NaCl* was spread uniformly over the area B and its radioactivity determined as described in the preceding section §3. The plots of count per minute against the amount of NaCl*, as shown in Fig. 3, lie almost on a straight line through the origin. The count of 10 mg NaCl* remained moreover unchanged, if piled up over 0.5 cm square area. This shows the proportionality of radioactivity to NaCl* quantity or the absence of self-absorption, assuring the quantitative determination of the amounts of chlorine deposition from the radioactivity measurement.

The specific radioactivity was calculated 1200 count per mg chlorine from the slope of the straight line and the purity 0.96 of the sample.

§ 5. Results.

It was found that 400 ct/min radiation of a NaCl* sample was
completely screened by all test pieces or no increase of count was observed if this sample was brought beneath them, except in the case of Ag plate, when the count was increased by 30% the radiation from below. The excess of observed count over the background count hence corresponds directly to the radioactivity of a single surface in every case except that of Ag, when the excess multiplied by 1/1.3 does.

**Table I.**

Results of \( HCl \) Treatment—(1)

Pressure of \( HCl \): 97.0 mmHg. Temperature: 250°C. Time: 8 hrs.

Pressure of uncondensed gas: 4.5 mmHg (0.57 L).

<table>
<thead>
<tr>
<th>Test pieces</th>
<th>Background count (I) ct/min.</th>
<th>Radioactivity count (II) ct/min.</th>
<th>Changes of surface of test pieces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>34</td>
<td>584</td>
<td>becomes gray</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>36</td>
<td>275</td>
<td>black color slightly faded</td>
</tr>
<tr>
<td>Fe</td>
<td>34</td>
<td>139</td>
<td>slightly covered by compact black</td>
</tr>
<tr>
<td>Ni</td>
<td>34</td>
<td>141</td>
<td>covered by compact black film</td>
</tr>
<tr>
<td>Graphite</td>
<td>34</td>
<td>134</td>
<td>unchanged</td>
</tr>
<tr>
<td>Au</td>
<td>34</td>
<td>62</td>
<td>unchanged</td>
</tr>
<tr>
<td>Pd</td>
<td>34</td>
<td>57</td>
<td>faint black tint before treatment</td>
</tr>
<tr>
<td>Cu</td>
<td>33</td>
<td>56</td>
<td>brownish</td>
</tr>
<tr>
<td>Ag</td>
<td>34</td>
<td>55</td>
<td>covered by white film</td>
</tr>
<tr>
<td>Pt</td>
<td>33</td>
<td>35</td>
<td>unchanged</td>
</tr>
</tbody>
</table>

**Table II.**

Relation between Excess Count and Standard Potential.

<table>
<thead>
<tr>
<th>Excess count ct/min.</th>
<th>Zn</th>
<th>Ni</th>
<th>Fe^{III}</th>
<th>Fe^{II}</th>
<th>Au^{III}</th>
<th>Au^{II}</th>
<th>Pd</th>
<th>Cu</th>
<th>Cu^{II}</th>
<th>Ag</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>107</td>
<td>105</td>
<td>28</td>
<td>23</td>
<td>22</td>
<td>16</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Standard potential Volt, 25°C: -0.76 -0.25 -0.44 -0.04 1.5 1.38 0.52 0.34 0.31 --

The results of radioactivity measurement are given in Tables I to V. "Radioactivity of test pieces" shows count per minute inclusive of background count directly measured by the method of §3. "Pressure
Research on Catalysis by Means of Radiochlorine Cl²⁺

### Table III.
Results of $HCl^*$ Treatment—(2)—$Fe_3O_4$ and $Fe$

<table>
<thead>
<tr>
<th>Test pieces</th>
<th>Background count (I) ct/min.</th>
<th>Radioactivity of test pieces ct/min.</th>
<th>Background count (II) ct/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fe_3O_4$</td>
<td>32</td>
<td>98</td>
<td>36</td>
</tr>
<tr>
<td>$Fe$</td>
<td>34</td>
<td>106</td>
<td>34</td>
</tr>
</tbody>
</table>

### Table IV.
Results of $HCl^*$ Treatment—(3)—Pt—Pt and Pd

<table>
<thead>
<tr>
<th>Test pieces</th>
<th>Background count (I) ct/min.</th>
<th>Radioactivity of test pieces ct/min.</th>
<th>Background count (II) ct/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt—Pt</td>
<td>32</td>
<td>152</td>
<td>34</td>
</tr>
<tr>
<td>Pd</td>
<td>34</td>
<td>47</td>
<td>32</td>
</tr>
<tr>
<td>Glass only</td>
<td>32</td>
<td>42</td>
<td>31</td>
</tr>
</tbody>
</table>

### Table V.
Results of $HCl^*$ Treatment—(4)—Pt—Pt

<table>
<thead>
<tr>
<th>Test pieces</th>
<th>Background count (I) ct/min.</th>
<th>Radioactivity of test pieces ct/min.</th>
<th>Background count (II) ct/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt—Pt</td>
<td>34</td>
<td>116</td>
<td>34</td>
</tr>
</tbody>
</table>

The pressure of uncondensed gas is that measured by McLeod gauge with tube $T_4$ cooled by liquid air as described in §2 and the figures in the parentheses give the volume it occupies. "Background count (I) and (II)" are respectively those measured before and after the determination of radioactivity of test pieces with the glass plate alone fitted to the counter, the data in the parentheses of column "Background count (II)"
being that measured without the glass plate. "Glass only" of Table IV gives the count of a glass plate of the same source to those which the films were evaporated on and treated by $HCl^*$ simultaneously with them. The last two columns of Table I show the changes of color and luster of the surface of test pieces caused by the $HCl^*$ treatment. Similar change were observed both in the cases of Table III and IV, although not given explicitly there.

We might proceed now in commenting on the Tables.

The experiment of Table I was carried out at the same temperature to that of the selective oxidation mentioned before but at the pressure twenty times as large as that of the latter experiment. The chlorine deposition is clearly detectable in every case except in that of Pt. The count of nobler metals is as shown by the Table I less than that of baser ones: the imparted radioactivity or the excess over the background count decreases with increasing standard potential as shown in Table II*) with an exception of gold.**

The experiment of Table III was carried out at one tenths the $HCl^*$ partial pressure to see if the considerable chlorine deposition, notwithstanding the observed indifference to $HCl$ referred to in the introduction, were due to the large partial pressure of $HCl^*$. The result is as shown in the Table that the deposition still persists. This results incorporated with the indifference might lead to the following alternative interpretations.

(i) The chloride practically screens off the catalytic activity of ferric oxide but has itself the same activity to replace it.

(ii) The chloride neither catalyses itself nor screens the activity of oxide due perhaps to incomplete coverage.

The alternative may be settled by experiment.

That bright Pt neither acquires radioactivity nor changes appearance by the treatment, is to be expected as shown below, if one assumes the chemisorption of chlorine in a monolayer of $10^{15}$, in order of magnitude, atoms or ions per cm$^2$ microscopic surface area at most.

Bowden and Rideal,*) observed the accessible area, as called by them, which is to be identified with the microscopic surface area, about twice as large as the apparent macroscopic surface area of bright Pt.

*) The excess count of Ag is corrected for the radioactivity of the back side.

**) It is plausible that the evaporated films of gold and palladium are exception in their behavior rather than rule of rolled plates of other materials. Cf. §3, Part II.

(*) Bowden, Proc. Roy. Soc. A 126, 107 (1929); A 125, 446 (1929).

Bowden and Rideal, ibid., A 130, 59 (1929).
Research on Catalysis by Means of Radiochlorine $^{36}$Cl

It follows now from the observed specific activity $1200 \text{ ct/min.mg} = \frac{1200 \times 35.46}{6.02 \times 10^{23} \times 10^{-3}} \text{ ct/min. Cl atom} = 10^{-16} \text{ ct/min. Cl atom}$, that the total radioactivity of bright Pt in our case is $10^{-16} \times 10^{15} \times 2 \times 2 = 0.4$ (ct/min) at most, one of two factors 2 being the macroscopic area of the plate, which certainly escapes the present radioactivity measurement.

But since the accessible area of Pt-Pt is 2000 times as large as the macroscopic one according to Bowden and Rideal, the plate of 4.9 cm$^2$ area would give $10^{-16} \times 10^{15} \times 4.9 \times 2000 = 1000$ ct/min at most: the radioactivity imparted may hence be measurable in this case.

Our results of bright Pt as well as that of Pt-Pt given in Table IV and V is in concordance with the above conclusion.

Best thanks of the authors are due to Mr. T. Matsui, Mr. Y. Naito, Assistant Professor T. Honda, Professor M. Ishibashi and the Radio-Isotopes Research Committee of Hokkaido University for their kind helps and encouragements.

The Research Institute for Catalysis
Hokkaido University
Sapporo, Japan.