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

Part I. Treatment with Radioactive Hydrogen Chloride

By

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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_3O_4 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

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***) The solution contains, besides, Na^+ , SO_4^{--} and decomposition products of $CHCl_3$ and CCl_4 .

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

(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,



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 T_1 which was connected to vacuum line through a normal joint and vacuum cock C_1 as shown in Fig. 1, added with 1 cc concentrated sulfuric acid, evacuated to 10^{-6} mmHg, then

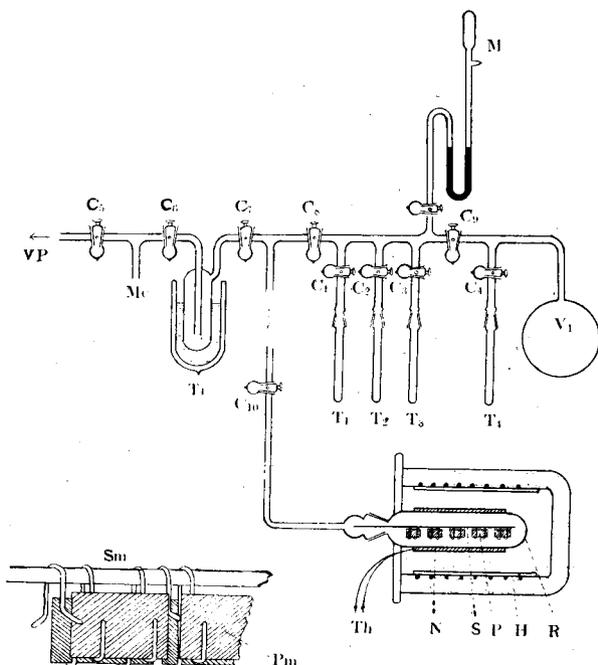


Fig. 1. Apparatus

- $C_1 \sim C_{10}$: Vacuum Cock,
- $T_1 \sim T_4$: Blind Tube,
- M: Manometer,
- Mc: McLeod Gauge,
- Tr: Trap,
- V_1 : 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_2 cooled by liquid air and having closed C_1 , HCl^* was further distilled into tube T_3 containing phosphorus pentoxide and then back again from T_3 to T_2 : this was repeated several times for drying HCl^* , which was finally distilled into tube T_4 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.

Plantinized platinum ($Pt-Pt$) was prepared as usual, from two round platinum plate of 2.5 cm diameter and 0.2 mm thickness by electrolysing 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 a 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, HCl^* stored in V_1 allowed to expand into R and the pressure read by manometer M. C_{10} was now closed and R left at the temperature for a recorded time. Tube T_4 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.

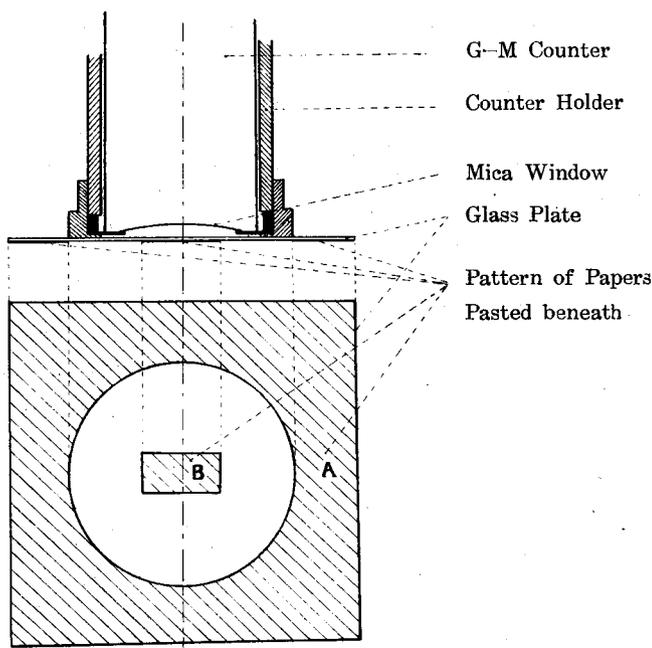


Fig. 2.

§ 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 ($1 \times 2 \text{ cm}^2$) 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.

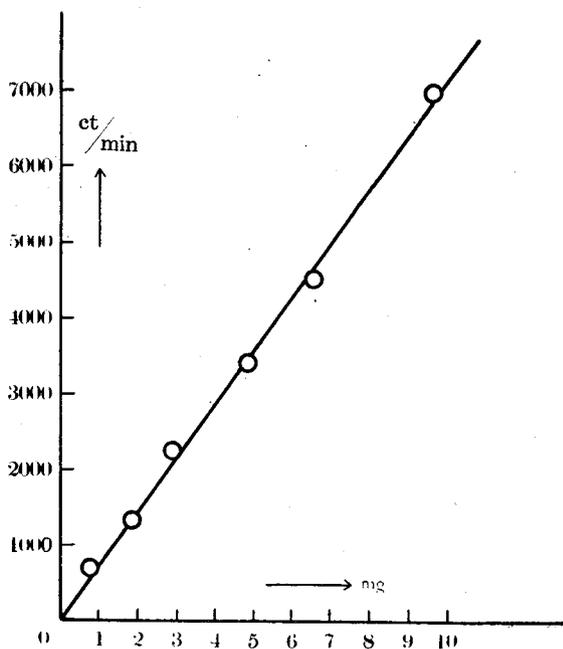


Fig. 3.

Radioactivity and Quantity of $NaCl^*$

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).

Test pieces	Background count (I) ct/min.	Radioactivity of test pieces ct/min.	Background count (II) ct/min.	Changes of surface of test pieces	
				color	luster
<i>Zn</i>	34	584	41 (34)	becomes gray	lost
<i>Fe₃O₄</i>	36	275	37 (34)	black color slightly faded	slightly lost
<i>Fe</i>	34	139	29	slightly covered by compact black film	slightly lost
<i>Ni</i>	34	141	34	covered by compact black film	slightly lost
<i>Graphite</i>	34	134	34	unchanged	unchanged
<i>Au</i>	34	62	33	unchanged	slightly lost
<i>Pd</i>	34	57	33	faint black tint before treatment becomes somewhat brownish	lost
<i>Cu</i>	33	56	34	—	lost
<i>Ag</i>	34	55	34	covered by white film	lost
<i>Pt</i>	33	35	36	unchanged	unchanged

TABLE II.
Relation between Excess Count and Standard Potential.

	<i>Zn</i>	<i>Ni</i>	<i>Fe^{II}</i>	<i>Fe^{III}</i>	<i>Au^I</i>	<i>Au^{III}</i>	<i>Pd</i>	<i>Cu^I</i>	<i>Cu^{II}</i>	<i>Ag</i>	<i>Pt</i>
Excess count ct/min.	550	107	105		28		23	22		16	0
Standard potential Volt, 25°C	-0.76	-0.25	-0.44	-0.04	1.5	1.38	—	0.52	0.34	0.81	—

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

TABLE III.

Results of HCl^* Treatment—(2)— Fe_3O_4 and Fe

Pressure of HCl^* : 10.2 mmHg. Temperature: 250°C. Time: 8 hrs.

Pressure of uncondensed gas: $10^{-1.6}$ mmHg (0.96 L).

Test pieces	Background count (I) ct/min.	Radioactivity of test pieces ct/min.	Background count (II) ct/min.
Fe_3O_4	32	98	36
Fe	34	106	34

TABLE IV.

Results of HCl^* Treatment—(3)— $Pt-Pt$ and Pd

Pressure of HCl^* : 9.8 mmHg. Temperature: 250°C. Time: 8 hrs.

Pressure of uncondensed gas: $10^{-2.3}$ mmHg (0.96 L).

Test pieces	Background count (I) ct/min.	Radioactivity of test pieces ct/min.	Background count (II) ct/min.
$Pt-Pt$	32	152	34
Pd	34	47	32
Glass only	32	42	31

TABLE V.

Results of HCl^* Treatment—(4)— $Pt-Pt$

Pressure of HCl^* : 99.3 mmHg. Temperature: 250°C. Time: 8 hrs.

Pressure of uncondensed gas: 10^{-3} mmHg (0.96 L).

Test pieces	Background count (I) ct/min.	Radioactivity of test pieces ct/min.	Background count (II) ct/min.
$Pt-Pt$	34	116	34

of uncondensed gas" is that measured by McLEOD gauge with tube T_1 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⁽³⁾ 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.

(3) BOWDEN, Proc. Roy. Soc. A 126, 107 (1930); A 125, 446 (1929).

BOWDEN and RIDEAL, *ibid.*, A 120, 59 (1928).

It follows now from the observed specific activity 1200 ct/min.mg = $1200 \times \frac{35.46}{6.02 \times 10^{23} \times 10^{-3}}$ ct/min. Cl atom = 10^{-16} 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,⁽³⁾ the plate of 4.9 cm² 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.

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