HOKKAIDO UNIVERSITY

Title	SYNTHESIS OF PRUSSIC ACID : Part 15 Study of Reaction Mechanism by Means of Radioactive Carbon
Author(s)	HORIUTI, Juro; TANAKA, Kazunori
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 4(3), 165-176
Issue Date	1957-03
Doc URL	https://hdl.handle.net/2115/24645
Type	departmental bulletin paper
File Information	4(3)_P165-176.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

SYNTHESIS OF PRUSSIC ACID

Part 15*)

Study of Reaction Mechanism by Means of Radioactive Carbon

By

Juro HORIUTI and Kazunori TANAKA**)

(Received July 1, 1956)

1. Introduction

The synthesis of prussic acid from carbon monoxide and ammonia has been investigated in this laboratory at ordinary pressure and at 600° to 750°C in the presence of the thoriated sulfuric acid catalyst supported on alumina (abbreviated to TS-catalyst).[1)-11)] It has thus been found that the reaction exclusively proceeds as,

$$2CO + NH_3 \longrightarrow HCN + CO_2 + H_2^{*)} \qquad (1)$$

and concluded from kinetic analysis that the initial complex of the rate-determining step is either identical or in partial equilibrium with $CO + NH_3$.[11,12)] It might be assumed in accordance with the conclusion that reaction (1) be governed by a step,

$$CO + NH_3 \longrightarrow HCN + H_2O \qquad (2.a)$$

followed by a quick one,

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (2.b)$$

It follows now from the assumption that in equilibrium of (1) carbon atoms of carbon dioxide will be found, if labelled e.g. by radioactive carbon atoms, to mix in those of carbon monoxide quicker than in those of hydrogen cyanide, provided that (2.a) and (2.b) were only steps which transfer carbon atoms between the molecules involved.

This conclusion has been thrown to the experimental test in the

*) Part 1 to Part 14 have been published in Japanese (Refs. 1-14).

**) J. H. and K. T.; Research Institute for Catalysis, Hokkaido University.

present work by means of radioactive carbon dioxide $C^{14}O_2$; the equilibrium mixture of the latter and other non-radioactive participants of (1) were circulated over TS-catalyst at 650°C at a total pressure slightly below one atm for a recorded time and then radioactivities of resultant carbon monoxide, carbon dioxide and hydrogen cyanide individually observed. The procedure and the results of the experiment are described below.

2. Material

Carbon monoxide was prepared from sodium formate and sulfuric acid in vacuum and dried over calcium chloride, sodium hydroxide and phosphorus pentoxide.

Cylinder ammonia was dried over sodium hydroxide and used either directly or after a fractional distillation.

Prussic acid was prepared by allowing potassium cyanide to react with 50 percent (by volume) aqueous sulfuric acid at room temperature in vacuum and dried over calcium chloride and phosphorus pentoxide. Prussic acid thus prepared contained three percent gas non-condensable at −80°C, presumably carbon dioxide.

The radioactive carbon dioxide was prepared by decomposing radioactive barium carbonate supplied by the US Atomic Energy Commission; 2.5 mgm latter sample was mixed with 3.7 gm ordinary barium carbonate and a portion of the latter mixture was diluted by five or six parts by weight of lead chloride and mildly heated in vacuum to liberate radioactive carbon dioxide.[15]

Hydrogen was prepared by electrolyzing aqueous sodium hydroxide, passed over nickel wire and then Pt-asbestos kept respectively at 350°C for removing oxygen and dried over calcium chloride and phosphorus pentoxide, and through a liquid air trap.

Oxygen was prepared by heating potassium permanganate in vacuum.

TS-catalyst was prepared from ammonium alum and thorium nitrate. Ten percent aqueous solution of ammonium alum was added with thorium nitrate so as to impart 3% ThO_2*) to Al_2O_3 by weight and then with 30% aqueous ammonia with stirring and white precipitate thus formed was filtered, dried at *ca.* 50°C for a few days and finally kept at 750°C for a few hours. Granules slightly larger than 20 meshes

*) A trace of iron was detected by potassium ferrocyanide.

were collected for use.

ZnO–Cr_2O_3 catalyst for conversion of carbon monoxide into carbon dioxide was prepared by calcinating the precipitate obtained by adding aqueous ammonia to a solution of zinc nitrate and chromic oxide.

3. Apparatus

Fig. 1 shows the apparatus used. The part surrounded by the dotted line is the circulation system, through which the equilibrium mixture is circulated over TS-catalyst in the reaction chamber R by means of a BRONSCHEDE's electromagnetic circulation pump Ep;*) T_1, T_2 and T_3 are traps for collecting, after the reaction, prussic acid,

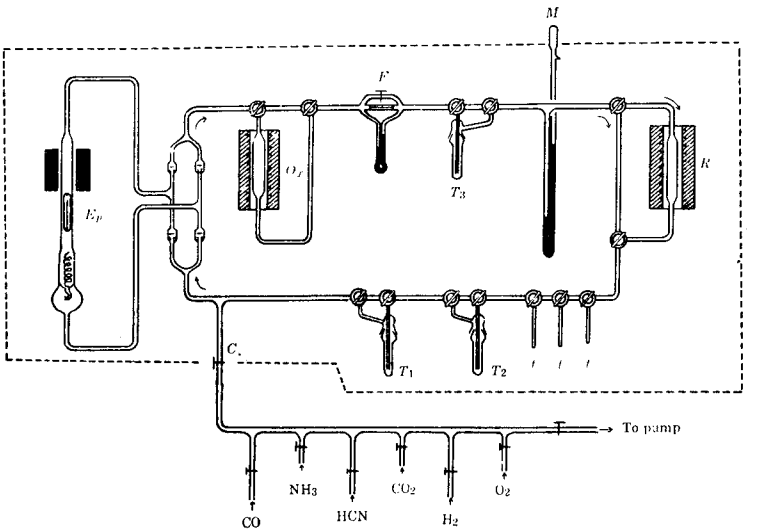

Fig. 1 Apparatus

M : manometer F : Flow meter
Ep: Electromagnetic circulation pump (Arrows show the direction of gas flow)
R : Reaction chamber Ox: CO-oxydizer
T_1, T_2, T_3: Trap t : Blind tube
◎ : Three way stopcock ⊢ : Two way stopcock

carbon dioxide and carbon monoxide oxydized by Ox, which contains conversion catalyst described in the previous section; t's are blind tubes for introducing prussic acid, carbon dioxide and ammonia into the

*) Cf. e. g. FARKAS & MELVILLE, *Experimental Methods in Gas Reactions*, London (1939) p. 54.

circuit by condensation, which are left communicated with the circuit, when the gas mixture is circulated. T_1, T_2, T_3, t's, Ox, and R are excluded from or included in the circuit by proper manipulations of three way stopcocks; the circuit including none of these parts will be called "the circuit" simply and that including R only "the circuit with R" and so on. C_* is a stopcock through which the circuit and the associated parts are evacuated or supplied with components of the gas mixture.

Fig. 2 shows the details of R provided with a thermocouple inserted at the catalyst layer.

Table 1 shows volums of respective parts of the apparatus.

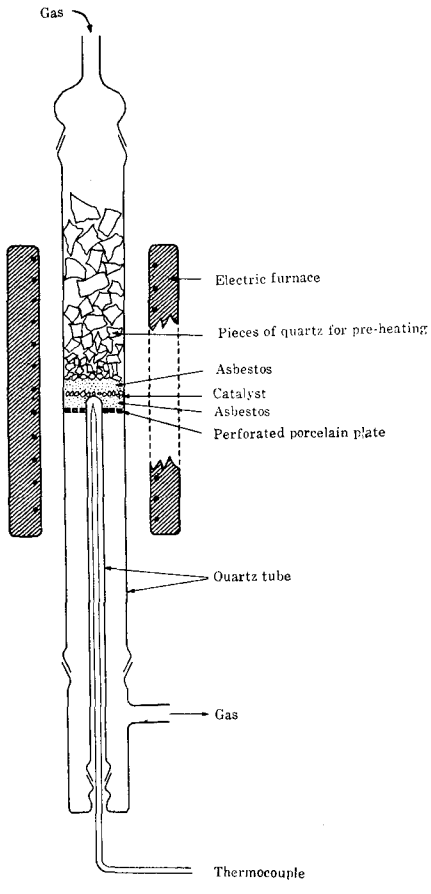

Fig. 2 Reaction Chamber R

4. Pretreatment of the Catalyst

It was found in the previous experiments[2] that, as the mixture of carbon monoxide and ammonia was passed over a fresh portion of TS-catalyst at 650°C, an appreciable amount of hydrogen sulfide was evolved, sulfur deposited, ammonia decomposed and hydrogen cyanide only poorly yielded; it took eight hours until the evolution of hydrogen sulfide considerably decreased and the yield of hydrogen cyanide simultaneously increased up to a

TABLE 1. Volume of Parts of the Apparatus

	Circuit	R	Ox	T_1	T_2	T_3	t's
Vol. (cc)	$367+0.0163\,P$ *)	156	127	75	82	82	17.6

*) P denotes pressure in mmHg.

steady value corresponding almost to the equilibrium composition.

The TS-catalyst in the present experiment was pretreated at the same temperature either by circulating a mixture of carbon monoxide and ammonia over it or passing fresh mixture one-through.

In the former case the temperature of R was raised gradually from room temperature to 650°C in $2\frac{1}{2}$ hours, while the mixture*) was circulated through R, kept constant at 650°C for several hours and then lowered to room temperature; this procedure was repeated twice in succession renewing the mixture every time, except that in the last round the temperature of R was raised to 650°C in vacuum before the mixture was circulated through it. Table 2 shows the partial pressures at the beginning of the circulation and the period of time in which R was kept at 650°C under circulation.

TABLE 2. Pretreatment with Gas Mixture

Partial Pressures and Time of Circulation

Round	1	2	3
Partial Press. of NH_3 (mmHg)	33	15	6.5
Partial Press. of CO (mmHg)	309	192	155
Time of Circulation (hrs.)	6.5	4	2

In the latter case of the one-through pretreatment carbon monoxide of the mixture was generated separately by dropping formic acid into warm concentrated sulfuric acid in (1), Fig. 3, passed over soda lime in (2) and introduced into the reservoir (3); the gas was pressed out from the reservoir by water, passed through concentrated aqueous caustic soda in (4), soda lime in (5) and CO-oxydizing catalyst heated at 300°C in (7) for removing a trace of oxygen, which retards the synthesis of prussic acid.[6] Ammonia was evaporated from the condensation of cylinder ammonia in trap (8) kept at *ca.* −30°C, passed over soda lime in (9). These components were mixed as shown in Fig. 3 and passed through R kept at 650°C through stopcocks Cp and Cq for 13 hours. The rate of flow of carbon monoxide was regulated at 10~20 cc/min and that of ammonia at 2~8 cc/min respectively by means of flow meters (6) and (10).

*) Ammonia used was not fractionally distilled.

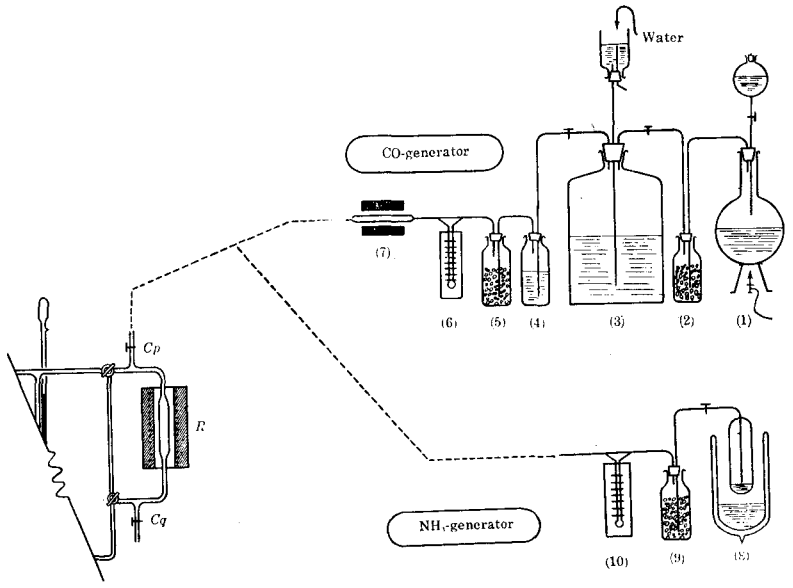

Fig. 3 One-through Pretreatment of Catalyst

The present one-through pretreatment was conducted at the same temperature as in the previous experiment,[2] but with much larger space velocity and for a longer time.

The evolution of hydrogen sulfide was followed throughout the present pretreatment by observing the turbidity caused by adding lead acetate to sodium hydroxide solution, which the exhaust gas from Cq, Fig. 3 was passed through and was renewed every 1~2 hours for the turbidity observation. Hydrogen sulfide evolution thus observed attained a maximum 1 or 2 hours after the temperature of the catalyst attained to 650°C and then decreased continuously down to a constant minute amonut after 6 hours.

5. Experimental Procedures

After the pretreatment of the catalyst, sulfuric acid was put into T_2, concentrated aqueous sodium hydroxide similarly into T_1 and T_3, these traps then evacuated for several minutes and turned off. The circuit with R, Ox and t's was evacuated to 10^{-5}~10^{-6} mmHg and then R, Ox and t's turned off from the circuit.

Radioactive carbon dioxide was now introduced into the circuit to a required amount observing M, condensed in one of t's, prussic acid

and ammonia similarly introduced and separately condensed in the other two t's and finally non-condensable gases, i. e. hydrogen and carbon monoxide introduced into the circuit in succession respectively to required amounts.

TABLE 3. Partial Pressures of the Equilibrium Mixture

mmHg at 27°C

Run	1, 3, 4, 5	2
CO	579.7	498.0
NH_3	26.1	22.5
HCN	39.8	34.2
$C^{14}O_2$	39.8	34.2
H_2	39.8	34.2
Total Press.	725.2	623.1

Table 3 shows the required amounts in the respective pressures at room temperature in the circut; they are the partial pressures of the equilibrium mixture which should result from the ammonia-carbon monoxide mixture of 1:10 mol ratio at 650°C as computed from the known equilibrium constant.[4] Pressure of each component gas could be adjusted by M to the calculated value of the Table within a few percent.

The contents of t's were now evaporated in turn into the non-condensable gas in the circuit, and the resultant mixture was circulated by means of Ep for two hours for securing the homogeneity. It was found preliminarily by analysis of a portion of the gas mixture after a 30 min circulation that its prussic acid content almost corresponded with that reckoned for a homogeneous mixture.

In the mean time, R was gradually heated up to 650°C and kept constant at the temperature. The mixture in the circuit with t's was now allowed to flow into R, the circulation instantly started and after a recorded time R was cut off to finish the run.

Carbon dioxide and prussic acid of the resultant mixture were fixed together in T_1 by circulating the mixture over aqueous sodium hydroxide in it. After the completion of absorption indicated by M as the cease of pressure decrease, the mixture was passed over sulfuric acid in T_2 for fixing ammonia there, similarly observing the end point

of absorption. Then in succession Ox was communicated with the circuit, T_1 and T_2 turned off, a small amount of oxygen added, T_3 communicated with the circuit and the residual gas circulated through Ox and T_3 in series. Four runs have thus been conducted, whereas in the other run (run 2, Table 3 and 4) Ox and T_3 were simultaneously communicated with the circuit before turning off T_1 and T_2 and the small amount of oxygen added finally. In every run the temperature of Ox was now gradually raised and maintained between 300~400°C for several hours to oxydize carbon monoxide and then to absorb carbon dioxide formed in aqueous sodium hydroxide in T_3, observing the pressure decrease similarly as above; this procedure of oxydation was repeated, preliminarily introducing a small amount of oxygen in every round, until the pressure decrease was no more observed.

Trap T_1 was removed from the apparatus, baryta water added, precipitate of barium carbonate formed was filtered. Prussic acid was precipitated from the filtrate as prussian blue or silver cyanide and filtered. Carbon dioxide in T_3 was similarly precipitated as that in T_1. These precipitates were dried in air-bath at 105°C, weighed and the radioactivity of each 21~24 mgm sample was measured in a definite brass cylindrical tray of 1.0 cm diameter and 0.4 cm height by Modell 16 GM counter supplied by the Scientific Research Institute Ltd. in Tokyo. Barium carbonate from carbon dioxide or carbon monoxide will be denoted by $[CO_2]$ or $[CO]$ respectively and prussian blue or silver cyanide from prussic acid by $[HCN]_P$ or $[HCN]_{Ag}$ similarly in what follows.

During every run thus conducted in succession the total pressure was found constant within 2 mmHg and the temperature of R similarly within a few degrees as observed by the thermocouple mentioned before.

6. Results

Table 4 shows the results of the experiment. The first column gives the number of runs, the second one the weight of TS-catalyst used, the third the observed total pressure, the forth the time of runs or that of circulation over the catalyst kept at 650°C and the fifth and the sixth the weight of the dry precipitates and the radioactivity of 21~24 mgm sample of them; observed weights of the respective precipitates are compared with those in parentheses calculated from the volumes of

TABLE 4. Results of Experiments

650°C, TS-Catalyst

Runs *)	Quantities of TS-Catalyst gm.	Total Pressure mmHg	Time of Runs min.	Precipitates								Relative Atomic Fractions of C^{14} after Runs		
				Weights (gm)				Radioactivities (ct min^{-1})						
				$[CO_2]$	$[HCN]_P$	$[HCN]_{Ag}$	$[CO]$	$[CO_2]$	$[HCN]_P$	$[HCN]_{Ag}$	$[CO]$	CO_2	HCN	CO
1 a)	0.2508	542~544	11	0.136 (0.123)	0.030 (0.030)		1.308 (1.36)	881	1570		23	68.61	29.60	1.79
2 b)	none	474~476	11	0.136 (0.109)	0.045 (0.026)		1.333 (1.24)	1412	9		7	99.36	0.14	0.50
3 b)	none	537~539	11	0.123 (0.123)		0.077 (0.083)	1.493 (1.36)	2004		90	12	96.48	2.94	0 58
4 c)	0.1935	532~534	14	0.165 (0.123)		0.072 (0.083)	1.486 (1.36)	894		980	26	56.40	41.96	1.64
5 d)	0.1935	537	14	0.136 (0.123)		0.072 (0.083)	1.491 (1.36)	1140		1131	22	59.10	39.76	1.14

*) Fractionated ammonia by distillation was used for every run except run 1.

a) Catalyst pretreated by circulating gas (cf. Section 4).

b) Catalyst removed leaving the asbestos bed as in the presence of the catalyst.

c) Catalyst pretreated in one-through gas (cf. Section 4).

d) Repetition of run 4 with the same portion of catalyst.

parts given in Table 1 and the pressures given in Tables 3 and 4. The last three columns of Table 4 show the relative magnitudes of the atomic fractions x^{CO_2}, x^{HCN} *) and x^{CO} of C^{14} in the precipitates, $[CO_2]$ etc. calculated as below, sum of them being normalized to 100.

The ratio x^{CO_2}/x^{CO} was taken directly as that of observed radioactivities. The x^{CO_2}/x^{HCN} was equated to the product of the ratio of the observed radioactivities and the inverse ratio of the numbers of carbon atoms contained in unit weight of the respective precipitates, i.e. as,

$$\frac{x^{CO_2}}{x^{HCN}} = \frac{R^{CO_2}M^{CO_2}m^{HCN}}{R^{HCN}M^{HCN}m^{CO_2}} \quad **), \tag{3}$$

where R^{CO_2} or R^{HCN} denotes the observed radioactivity, M^{CO_2} or M^{HCN} the molecular weight of the dry precipitate and m^{CO_2} or m^{HCN} the number of carbon atoms contained in the molecule respectively. The above equation states particularly for $[HCN]_P$ that,

$$\frac{x^{CO_2}}{x^{HCN}} = \frac{R^{CO_2}\cdot 197.4\times 18}{R^{HCN}\cdot 859.3\times 1} = 4.13\,\frac{R^{CO_2}}{R^{HCN}} \tag{4}$$

taking the molecular formula of prussian blue as $Fe_4[Fe(CN)_6]_3$.

We will proceed commenting on the runs in Table 4.

Run 1 gave an unexpected result that the increase of x^{HCN} was appreciable and even larger than that of x^{CO}. Run 2 was conducted for examining whether the x^{HCN}-increase was caused by something other than TS-catalyst in R, by removing the catalyst alone, leaving other contents as they were. The result was that the increase of x^{HCN} as well as that of x^{CO} was extremely smaller than in run 1, showing that the catalyst itself was responsible for the result of run 1. The result of

*) The x^{HCN} refers to either $[HCN]_P$ or $[HCN]_{Ag}$.

**) The radioactivity R observed right above a cylindrical pile of a radioactive sample of definite weight W is given as, $R=R_0\int_0^W \exp(-\mu D)\,dw$, where w is the weight of the sample contained above a horizontal plane of depth D from the top of the cylinder, R_0 the radioactivity of unit weight without absorption and μ the absorption coefficient. Expressing D as $D=w/\rho A$ in terms of the apparent density ρ of the dry precipitate and the horizontal sectional area A of the cylinder, we have $R=R_0\int_0^W \exp\left(-\frac{\mu w}{\rho A}\right)dw$. Assuming μ/ρ common to all samples, because of the approximately common value of the mass absorption coefficient, the value of the integral is the same for the same values of W and A, so that R is proportional to R_0.
R having now been found practically constant by varying W from 16 to 21 mgm, a small difference of W in our observation (21~24 mgm) does not matter the validity of (3).

run 2 was further ascertained by its repetition, run 3.

Run 4 was conducted with 0.1935 gm new portion of catalyst which was pretreated by one-through gas for fully activating it in accordance with the previous work as described in Section 4. The run was conducted for 14 minutes, adjusting the product of the time and the catalyst quantity equal to that of run 1. The result of this run and that of the repetition, run 5 unanimously confirm that of run 1.

We see from Table 4 that the observed weights of the precipitates are not quite in agreement with the calculated ones. The cause of this discrepancy is not clear but since the results of runs 2 and 3 compared with those of other runs amply assure a practically complete separation of components of the mixture which is essential in the present research, it was not tried to inquire into its cause nor to eliminate it.

7. Conclusion

It is concluded that TS-catalyst causes the carbon atoms of carbon dioxide to enter into hydrogen cyanide much more quickly than into carbon monoxide or that they enter into prussic acid directly from carbon dioxide but not via carbon monoxide on the contrary to the initial expectation.

There might exist two ways of accounting for this exprimental result. One of them is to attribute the quick carbon exchange between carbon dioxide and hydrogen cyanide to the sequence of steps appropriated to the overall reaction (1). If then, the sequence of (2. a) and (2. b) must be replaced by some other, e. g.

$$\left.\begin{aligned} CO + NH_3 &\longrightarrow HCONH_2 \text{ (rate determining step)} \\ CO + HCONH_2 &\longrightarrow C_2O_2NH + H_2 \\ C_2O_2NH &\longrightarrow HCN + CO_2, \end{aligned}\right\} \quad (5)$$

whose third step is rapider than the second one, so that carbon atoms in carbon dioxide enter into hydrogen cyanide quicker than into carbon monoxide.

The other way is to attribute the quick exchange to a separate step or a sequence of steps, not included in the sequence of the overall reaction (1). In this case the sequence of (2. a) and (2. b) is not necessarily excluded.

Summary

1. An equilibrium mixture of CO, NH_3, HCN, radioactive $C^{14}O_2$ and H_2 with respect to the reactien,

$$2CO + NH_3 \longrightarrow HCN + CO_2 + H_2 ,$$

was circulated over the HCN synthesis catalyst, i.e., the thoriated sulfuric acid catalyst supported on alumina, at 650°C for 11 or 14 minutes and the radioactivities of CO, HCN and CO_2 were individually observed.

2. The increase of the radioactivity of HCN was found much larger than that of CO or, in other words, carbon atoms are exchanged between HCN and CO_2 directly but not *via* CO.

3. The above result excludes the sequence of steps,

$$CO + NH_3 \longrightarrow HCN + H_2O \quad \text{(rate-determining step)}$$
$$H_2O + CO \longrightarrow H_2 + CO_2$$

appropriated to the above overall reaction, unless a separate step or sequence of steps, not included in the above sequence, be responsible for the exchange.

References

1) HORIUTI and KINOSHITA, Shokubai (Catalyst) No. 4, 53 (1948).
2) KINOSHITA, YANO and SATO, *ibid.* No. 5, 60 (1949).
3) YANO and KANAI, *ibid.* No. 7, 1 (1951).
4) HORIUTI, YANO and KANAI, *ibid.* No. 7, 8 (1951).
5) NAKAMURA, *ibid.* No. 7, 17 (1951).
6) YANO, *ibid.* No. 7, 21 (1951).
7) YANO and HORIUTI, *ibid.* No. 7, 32 (1951).
8) HORIUTI, *ibid.* No. 8, 1 (1952).
9) HORIUTI and TANABE, *ibid.* No. 8, 24 (1952); see also, this Journal Vol. 1, No. 3, 117 (1951).
10) YANO and ISHIZUKA, Shokubai (Catalyst) No. 10, 43 (1954).
11) YANO and ISHIZUKA, *ibid.* No. 10, 51 (1954).
12) HORIUTI and YAMAGUCHI, *ibid.* No. 10, 60 (1954).
13) HORIUTI, SATO, WATANABE and ISHIZUKA, *ibid.* No. 13, 1 (1956).
14) HORIUTI and SATO, *ibid.* No. 14, 7 (1957).
15) ZWIEBEL, TURKEVICH and MILLER, J. Am. Chem. Soc. **71**, 376 (1949).

Note: References 1) to 14) are written in Japanese.