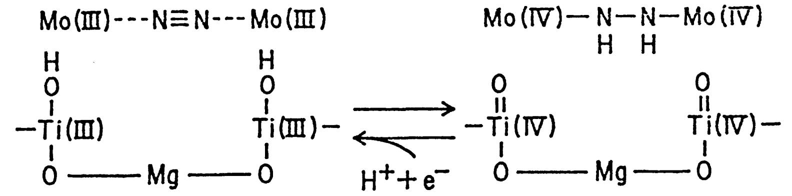
CHEMISTRY LETTERS, pp. 1871-1874, 1983. © The Chemical Society of Japan 1983

DIRECT SYNTHESIS OF HYDRAZINE OVER METAL OXIDE CATALYSTS UNDER SILENT DISCHARGE

Koshiro MIYAHARA
Research Institute for Catalysis, Hokkaido University, Sapporo 060

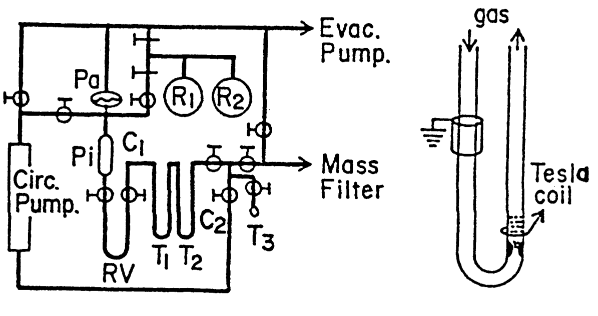
The direct synthesis of hydrazine over solid surfaces was performed by means of various metal oxide catalysts and activation of gas by silent discharge at room temperature.

The hydrogenation of molecular nitrogen to hydrazine has been investigated by means of the decomposition of metal complexes of molecular nitrogen,1) the photocatalysis with wet titania in nitrogen atmosphere2) and homogeneous catalysis in liquid phase3) *etc* . Summerizing the results of these experiments, we see that the activation of molecular nitrogen by its coordination to appropriate metal ions and the processes of protonation accompanying the redox of metal ions are necessary for the hydrazine synthesis, as illustrated by the mechanism proposed by Shilov *et al.*3) for the catalytic activity of mixed hydroxides of Mo, Ti, and Mg in a liquid phase.



(1)

These results as well as the high catalytic activity of molybdenum oxide supported on titania for olefin metathesis4) and that of magnesia for olefin hydrogenation5) suggest the applicability of these metal oxides for the synthesis of hydrazine in gas phase with an appropriate process for protonation. This expectation was examined in this report with respect to the catalyst for olefin metathesis4) and other typical metal oxide catalysts under silent discharge of gas.



a) b)

Fig. 1.
The schematic diagram of a): the reaction apparatus and b): the reaction vessel.

The reaction apparatus is a usual circulation system of *ca.* 220 cm^3 volume as shown in Figs. 1,a and b, where all of the stop valves were of greeseless, otherwise the apparatus could not be evacuated by dissolution of hydrazine into greese. The reaction vessel was a quartz U-tube of 6 mm inner diameter, in which the catalyst was set as shown in Fig. 1,b. The silent discharge from a Tesla coil of *ca*. 16 WH was applied to the reactant gas of less than *ca*. 1×10^3 Pa by setting the poles of discharge so as to limit the glow of discharge to the gas inlet side of the catalyst bed. The total pressure of gas was followed by strain gauge, Pa: TOYODA DD 102A, while Pilanyi gauge, Pi, was used for the flash desorption experiment.

A mass filter, NAG-515 of NEVA, was used for the gas analysis at $2.5–4.0 \times 10^{-5}$ Pa. The reaction products contained water, carbon monooxide, dioxide and hydrocarbons *etc*. and, hence, $^{15}N_2$ was used for the reaction to make easy the gas analysis. The utility of the mass filter for the analysis of hydrazine and ammonia was ascertained by the use of their mixtures.

After the reaction of 10-15 min. with the liquid nitrogen trap T_1, the valves, C_1 and C_2 in Fig. 1,a, were closed for the complete evacuation of the trap T_1. The condensed product in the trap T_1 was then outgassed by transferring it into the trap T_2 and it was finally vaporized and flowed into the mass filter. The use of $^{15}N_2$ gas and such a careful outgassing of the condensed product enabled us to perform the accurate gas analysis. The analysis was further made sure by the use of the trap T_3 charged with $KMnO_4$ crystallites, with which only hydrazine was decomposed completely at room temperature.

The results of the experiment with powdered catalysts and a mixture of $H_2/N_2 \cong 2$ are given in Table 1. The catalysts mixed with a few mol% oxide were made by the impregnation of main metal oxide with aqueous solution of appropriate metal salts, except their halogenides. The dried catalyst sample was calcined in air at 600 °C and *ca*. 0.1 g was charged in the reaction vessel and evacuated up to 600 °C for 10 min. to get the flash desorption spectrum. Under the silent discharge, the reaction with the H_2/N_2 mixture was steady and 0 th order with respect to the total pressure, but a slight decrease of the pressure was observed only in the early stage of the reaction with N_2 alone. Table 1 shows the real possibility of the synthesis of hydrazine over oxide catalysts, in spite of its poor selectivity in the steady reaction.

Table 1. The reaction over powdered metal oxide catalysts.

Metal oxide	Activity	Selectivity (NH_3:N_2H_4:CH_4N_2 mol%)					
	p/ t(Pa/s)	with $H_2/^{15}N_2$ mixture			with $^{15}N_2$ alone		
None	0.18	100	0	0	–	–	–
SiO_2 gel	0.20	87	11	2	0	20	80
MoO_3/ TiO_2/$Mg(OH)_2$	0.21	96	4	0	0	9	91
am TiO_2/$Mg(OH)_2$	0.28	91	9	0	0	42	58
MoO_3/Mg oxalate	0.28	86	0	14	0	0	100
am TiO_2	0.25	80	11	9	0	0	100
$Mg(OH)_2$	0.32	92	8	0	0	80	20
Al_2O_3	0.20	72	28	0	0	46	54
SiO_2/Al_2O_3	0.18	88	12	0	0	12	88
SiO_2/MgO	0.23	23	17	60	8	24	68

Irrespective of the sort of the catalyst, hydrocarbon up to C_6 was formed under the silent discharge of hydrogen gas, suggesting the incorporation of carbonaceous impurity in the metal oxides. The fact that the gas evacuated from the liquid nitrogen trap T_1 was mainly ethylene, suggests the synthesis of hydrocarbon proceeds through the intermediate, $-CH_2$, of FT synthesis. In the case of the presence of $^{15}N_2$, the hydrocarbon synthesis was suppressed and ,instead, the peak at m/e = 46 appeared in the mass spectrum of the product. The peak at m/e = 46 was identified as diaziridine,6) $CH_2N_2H_2$, because the peak at m/e = 46 disappeared and the peak at m/e = 44 grew instead by the change of the reactant from $^{15}N_2$ to $^{14}N_2$ and, furthermore, it was stable for the treatment at the trap T_3. It seems to be formed by the scavenging effect of active molecular nitrogen for the intermediate, $-CH_2$, of the FT synthesis. The reactivity of the carbonaceous impurity in metal oxides will be reported elsewhere. Hydrogen cyanide and/or amino acids, reported as to be formed remarkably from the gas mixture of nitrogen or ammonia and hydrocarbon under the discharge or over heated silicagel,7) were never observed in the present experiment.

According to the result that the activity given in Table 1 was mainly affected by the intensity of the glow of discharge, but not by the surface area of the catalyst, and, furthermore, the large amount of product adsorbed on the catalyst affects the measurement of the activity and selectivity, the catalysts were changed to quartz pieces and MgO crystallites from Tateho Chem. Co. Ltd., both of 10-16 mesh. They were preliminarily calcined in air at 1200 °C for one hour or more to suppress the incorporation of the carbonaceous impurity as well as the adsorption of products. The calcined quartz pieces and MgO crystallites were modified by metal oxides by wetting their 0.6 g with an aqueous solution of an appropriate metal salt (*ca.* 5×10^{-3} g cm^{-3}) and calcination at 600 °C. The results are given in Table 2, where we see that the formation of CH_4N_2 was

Table 2. The reaction over quartz pieces and MgO crystallites.

Catalyst		H_2/N_2 mol ratio	Activity $\Delta p/\Delta t$(Pa/s)	Selectivity(NH_3:N_2H_4:CH_4N_2 mol%)					
				with $H_2/^{15}N_2$ mixture			with $^{15}N_2$ alone		
Quartz	None	1.48	0.22	79	21	0	8	86	6
	V	1.68	0.21	74	26	0	10	85	5
	Cr	1.37	0.19	85	15	0	0	99	1
	Co	1.25	0.20	73	27	0	14	84	2
	Ti	1.32	0.15	58	42	0	0	96	4
	K	1.19	0.14	64	36	0	0	98	2
MgO	None	1.39	0.15	74	26	0	16	84	0
	Mo	1.61	0.13	83	17	0	0	98	2
	V	1.09	0.15	76	24	0	0	98	2
	Cr	1.35	0.17	77	23	0	7	89	4
	Co	1.61	0.13	66	34	0	0	96	4
	Ti	1.92	0.15	77	23	0	4	92	4
	K	1.45	0.22	75	25	0	12	86	2

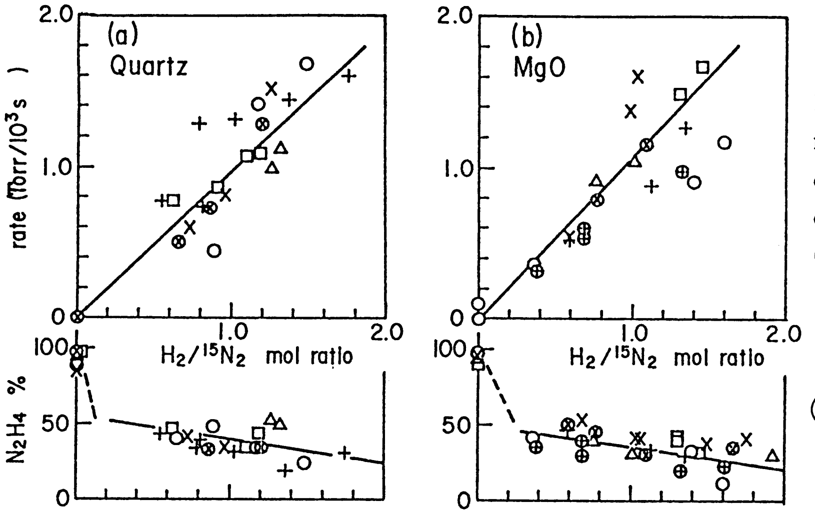


Fig. 2. The dependence of the activity and selectivity for hydrazine synthesis on the mixing ratio of H_2 to $^{15}N_2$ over a): quartz and b): MgO crystal.
(○ : unmodified, ⊕ : Mo, ⊗ : V, + : Cr, × : Co, △ : Ti, □ : K)

(Torr = 133.32 Pa)

effectively supressed. The adsorpion of product on these catalysts was practically negligible as proved by the flash desorption spectra of the used catalysts. It was found, furthermore, as given in Figs. 2,a and b, that the activity and the selectivity for hydrazine synthesis depend on the mixing ratio of nitrogen to hydrogen. The isotopic equilibration in nitrogen gas was easily caused by application of silent discharge. And, hence, the high selectivity for hydrazine formation with nitrogen alone, indicates that the activated nitrogen molecules are effectively formed on the metal oxide surface and easily protonated by surface OH groups as illustrated by the Shilov's mechanism (1).

So far as the present experiments concern, the sort of metal oxide does not affect the activity and selectivity for hydrazine formation from the mixture of nitrogen and hydrogen, but affect the formation of diaziridine in the case of nitrogen gas alone. The basic nature of the catalyst looks like to provide surface OH to form hydrazine and suppress the formation of CH_2-intermediate from carbonaceous impurity of the catalyst. Hydrogen is consumed preferentially to form ammonia, while, as seen from the reproducible formation of hydrazine after repeated use of the catalyst, it is partly used to regenerate surface OH, resulting in the direct synthesis of hydrazine.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) *E.g.* Y. Miura and A. Yamamoto, Chem. Lett., 1978, 937.
2) G. N. Schrauzer and T. D. Guth, J. Am. Chem. Soc., 99, 7189 (1977).
3) A. E. Shilov, N. T. Denisov, O. N. Efimov, N. T. Shuvaliva, and A. K. Shilova, Nature, 231, 480 (1971).
4) Ka. Tanaka, K. Tanaka, and K. Miyahara, Chem. Lett., 1980, 623.
5) K. Miyahara, Y. Murata, I. Toyoshima, Y. Tanaka, and T. Yokyama, J. Catal., 68, 186 (1981).
6) S. I. Zones, M. R. Palmer, J. G. Palmer, J.M. Doemeny, and G. N. Schrauzer, J. Am. Chem. Soc., 100, 2113 (1978).
7) *E.g.* M. Calvin, Chemical Evolution-molecular evolution towards the origin of living systems on the earth and elsewhere, Oxford University Press (1969), Chap. 6.

(Received August 31, 1983)