Bull. Chem. Soc. Jpn., **53**, 3184—3188 (1980) [Vol. 53, No. 11

Nitrogen Determination by Pyrolysis Using Steam. I.

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(Received January 31, 1980)

Pyrolysis of nitrogen compounds with use of steam and $FeCl_3$–Al_2O_3 catalyst was investigated in detail in order to develop a new method for nitrogen determination. The catalyst was prepared by mixing an aqueous $FeCl_3$ solution and porous active Al_2O_3 for column chromatography and drying the mixture. A sample solution containing nitrogen was added to the catalyst in a boat and was then covered with an additional catalyst after removal of the solvent, leaving the sample adsorbed on the catalyst. The boat was then inserted into a pyrolysis tube, the sample being pyrolyzed in the presence of steam also used as carrier gas. The nitrogen in the sample converted into ammonia by the pyrolysis reaction was determined by titration after steam distillation under alkaline conditions. The nitrogen compounds except for N–O and N–N bonded compounds were converted quantitatively into ammonia by the pyrolysis under optimum conditions. The reaction was applied to the determination of nitrogen in various compounds.

Nitrogen determination of organic compounds was carried out mainly by the classical Kjeldahl, Dumas and ter Meulen method. Modification of their method has been investigated. Hozumi and Kirsten$^{1)}$ reported the sealed tube method. Microcoulometry combined with hydrogenation of nitrogen compounds$^{2)}$ and chemiluminescence measurement of nitrogen monoxide with ozone$^{3)}$ were applied to nitrogen determination. Nitrogen in coke was determined by the semimicro gasification method$^{4)}$ using steam as a carrier gas.

A new method for nitrogen determination of organic compounds is described in this paper. Its principle is based on the fact that nitrogen compounds are converted into ammonia by pyrolysis using $FeCl_3$–Al_2O_3 catalyst in the presence of steam.

Experimental

Materials. Porous active aluminium oxides (Al_2O_3) for column chromatography (Merck) were used. Methyl Red–Methylene Blue mixed indicator was used for acidimetric titration. Other reagents were of reagent grade.

Apparatus. The apparatus for pyrolysis is shown in Fig. 1. The nitrogen contents in the reagents were determined with a microcoulometric titrating system (Model TN-01, Mitsubishi Chemical Industrial Co. Ltd.) or a Kjeldahl digestion and distillation apparatus.

Ammonia converted from the nitrogen compounds by pyrolysis was identified by gas chromatography (Shimadzu GC-4CMPF) with a nitrogen-selective detector (Envirotech Corp., Dohmann Microcoulometric Titration System-10) based on the investigation by Martin.$^{2)}$ A glass column, length 1 m, i.d. 3 mm, packed with 10% by weight PEG-20M (Gas Chro. Industrial Co. Ltd.) on Chromosorb-W precoated with 5% of KOH was used, argon being used as carrier gas at 40 ml/min. A glass precolumn (3 mm i.d. × 90 mm) installed in the sample inlet zone of the gas chromatograph was packed with soda lime and heated at 200 °C to release the basic compounds in the samples.

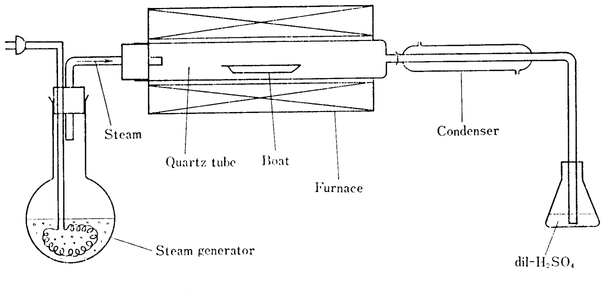

Fig. 1. Schematic diagram of apparatus for pyrolysis.

Preparation of Catalysts. Aqueous $FeCl_3$ solutions (50 ml) of various concentrations were added to Al_2O_3 (100 g), thoroughly mixed with a pestle and dried at 60 °C for 5 h. It is desirable to prepare the catalysts as required. Otherwise they should be stored in a desiccator containing silica gel.

Procedure. The catalyst (1.5 g) was uniformly distributed in an alumina boat (Japan Chemical Ceramic Co. Ltd., SSA-H5B). A sample solution of 0.5 ml containing approximately 1 mg of nitrogen dissolved with a suitable solvent was added to the catalyst with a micro pipette (Toa Medical Electronic Co. Ltd., Type 1058-F500) and dried at 60 °C in order to remove the solvent. The catalyst supporting the sample was covered uniformly with an additional catalyst (2.0 g). The boat was pushed with a stainless steel wire attached to the tail of the boat into a quartz pyrolysis tube ($28.5\phi \times 475$ mm), heated at 700—1000 °C in a furnace. Steam of 2.5 g/min, regulated with a Slidac, was immediately supplied from a steam generator for 10 min by connecting a hose to the open end of the pyrolysis tube. The pyrolyzed products were carried by the steam through a condenser to a flask containing dilute H_2SO_4 for absorption of ammonia in the reaction products. Ammonia was determined by the conventional titration method after steam distillation under alkaline conditions, since acidic materials such as HCl are produced during the course of pyrolysis by the decomposition of $FeCl_3$ and the sample. In order to obtain a blank value, the same procedure was carried out for the catalyst without sample.

Results and Discussion

Nitrogen compounds are classified into three types$^{5)}$—Type I: N–H and N–C bonded; Type II: N–O bonded; and Type III: N–N bonded. Ammonium sulfate, urea, pyridine, aniline, *p*-dinitrobenzene, and azobenzene were selected as typical compounds.

Identification of Ammonia by Gas Chromatography with Nitrogen-selective Detector. Since the method is based on the fact that nitrogen compounds are converted into ammonia by the pyrolysis reaction utilizing the $FeCl_3$–Al_2O_3 catalyst, the detection and identification of ammonia by gas chromatography with a nitrogen-selective detector would help confirm the validity of the method.

Samples for chromatographic analysis were prepared

TABLE 1. EFFECT OF ALUMINIUM OXIDE PROPERTIES ON PYROLYSIS

No.	Properties of Al_2O_3			Concentration of $FeCl_3(Fe/Al_2O_3)$/wt%	Recovery of N/%			
	Activity[a]	Pore diameter/Å	Acidity		Pyridine	*p*-Dinitrobenzene	Azobenzene	Urea
1	I	90	Neutral	1	76.1	57.6	82.3	100.4
				2	93.2	73.8	91.6	98.7
				4	99.3	76.3	84.9	81.6
				6	95.7	87.0	72.3	83.4
2	I	90	Aacidic	1	86.3	79.4	88.0	95.5
				2	97.2	89.8	92.3	86.7
				4	97.7	91.9	81.0	81.2
				6	96.5	85.5	61.2	78.3
3	I	90	Basic	1	—[b]	80.2	74.7	98.0
				2	92.6	85.2	90.1	96.2
				4	94.9	88.1	85.5	92.9
				6	95.3	85.4	75.3	90.1
4	I	60	Basic	1	70.5	63.4	76.7	97.6
				2	89.1	73.3	78.0	99.0
				4	97.7	88.8	83.8	94.8
				6	95.9	87.9	63.0	79.2
5	I	150	Basic	1	—[b]	87.0	82.6	99.5
				2	83.7	85.9	88.6	97.0
				4	81.7	87.2	84.2	98.3
				6	81.4	90.0	56.2	97.9
6	II—III	90	Basic	1	—[b]	74.7	71.0	98.6
				2	93.4	85.6	84.7	98.7
				4	96.0	90.0	81.3	91.2
				6	96.7	84.7	73.7	91.3

a) Determined according to the method of Brockmann and Schodder.[6] b) End point not clear due to the presence of unreacted pyridine.

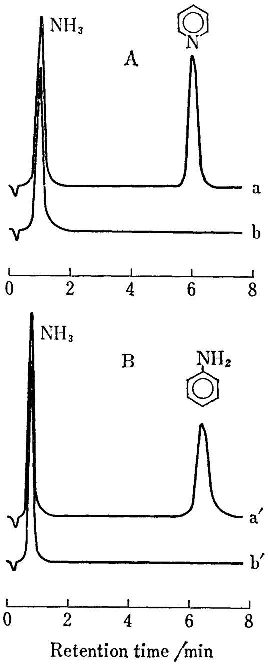

Fig. 2. Identification of ammonia by gas chromatography with nitrogen-selective detector.
A; Column temperature: 100 °C, a: standard sample (ammonium sulfate 100 ng N, pyridine 100 ng N), b: reaction products of pyridine at 800 °C, B; column temperature: 170 °C, a′: standard sample (ammonium sulfate 100 ng N, aniline 100 ng N), b′: reaction products of aniline at 800 °C.

as follows. The pyrolyzed products of 1 mg N of pyridine or aniline, absorbed in dilute H_2SO_4, were distilled. The distillate was neutralized with slight excess of acid (H_2SO_4) in an adaptor, then codensed to 10 ml. If the nitrogen in the pyridine or aniline is quantitatively recovered as ammonia, 100 ng/μl of nitrogen should be contained in the condensed solution.

The sample of 1 μl (100 ng N) was injected through the inlet of the gas chromatograph and the chromatogram obtained was compared with that of a standard sample (Fig. 2). Peaks of both pyridine and aniline (chromatograms A and B) disappeared, only that of ammonia appearing after the pyrolysis. The peak height of ammonia converted from pyridine or aniline was nearly the same as that of ammonia (100 ng N) in a standard sample.

The results indicate that both pyridine and aniline are converted into ammonia giving no other basic nitrogen compounds detectable with a nitrogen-selective detector. The conventional acidimetric titration is simpler and more precise for determination of ammonia as compared with chromatographic determination when only ammonia exists as a basic compounds.

Effect of Aluminium Oxide Properties. Aluminium oxides used were porous sorbents for column chromatography (particle size: 0.04—0.15 mm). The properties of aluminium oxides (Merck) are summarized in Table 1, together with catalytic efficiencies. The concentration of $FeCl_3$ supported on Al_2O_3 was in the range 1—6% of Fe/Al_2O_3. The temperature for the pyrolysis was 800 °C, the steam flow rate being 2.5 g/min.

Table 2. Effects of the amount of catalyst and the heating temperature on pyrolysis

Compound	Amount of catalyst/g	Recovery of N/%				
		600 °C	700 °C	800 °C	900 °C	1000 °C
Pyridine	0	—[a]	—[a]	—[a]	—[a]	—[a]
	1	—[a]	81.3	90.2	90.4	82.0
	2	54.7	94.7	99.3	101.3	88.6
	3	48.7	90.3	99.3	100.6	82.8
p-Dinitrobenzene	0	64.2	61.0	55.1	48.0	57.1
	1	45.6	68.3	63.0	62.8	80.9
	2	33.8	69.9	76.3	59.4	68.5
	3	33.6	71.2	77.6	56.0	51.0
Azobenzene	0	38.5	56.6	68.0	59.1	51.0
	1	51.0	75.3	82.4	74.1	50.6
	2	38.2	62.3	84.9	74.7	56.9
	3	31.6	71.9	82.3	68.4	56.4
Urea	0	32.3	93.0	97.6	96.9	94.8
	1	72.6	88.8	93.6	82.3	62.0
	2	43.4	89.4	81.6	69.1	46.3
	3	41.0	91.9	81.5	56.3	35.9
Ammonium sulfate	0	73.8	101.1	96.8	89.3	77.2
	1	68.4	98.3	90.4	77.7	59.2
	2	61.4	79.9	80.9	53.8	38.1
	3	70.5	70.5	69.5	38.2	27.7

a) End point not clear due to the presence of unreacted pyridine.

The nitrogen in pyridine was recovered quantitatively by 4%-Fe/Al_2O_3 except for No. 5 whose pore size is the largest among the Al_2O_3 we used. The reason for the low recovery of pyridine by No. 5 has not been clarified. We assume the removal of some pyridine from the catalyst during the drying process due to larger pore size (low adsorptivity for pyridine), since 8-quinolinole (oxine), having lower vapor pressure than pyridine, was recovered quantitatively.

The activity and acidity of Al_2O_3 did not remarkably affect the recovery of the nitrogen compounds. On the other hand, both *p*-dinitrobenzene and azobenzene could not be recovered quantitatively under the conditions in Table 1.

In urea (Type I), which is the same as pyridine except for the fact that it contains only one carbon atom in a molecule, the recovery increased as $FeCl_3$ concentration decreased except for No. 5. Iron(III) chloride supported on Al_2O_3 is assumed to undergo oxidation to Fe_xO_y during the course of pyrolysis, urea or its intermediates being considered to be partly oxidized due to the excessive presence of Fe_xO_y causing the low recovery of ammonia. Low concentration of $FeCl_3$ is recommended. The results obtained for No. 1 Al_2O_3 which supported no $FeCl_3$ showed a 95.0% recovery, which is a little low.

Effect of the Amount of Catalyst and Heating Temperature. The effect of the amount of the additional catalyst, covering the sample supported on the catalyst (1.5 g) in the boat, and that of heating temperature in the hot zone on the recovery of pyridine, *p*-dinitrobenzene, azobenzene, urea, and ammonium sulfate were studied. The results are given in Table 2. The concentration of the catalyst was 4%-Fe/Al_2O_3.

Pyridine was recovered quantitatively by the catalyst of 2 and 3 g at 800 and 900 °C, respectively. Below 700 °C the pyrolysis of pyridine could not be completed. Presumably oxidation took place to reduce the recovery at temperatures above 1000 °C.

Although nitro and N–N bonded compounds such as *p*-dinitrobenzene and azobenzene have not been determined quantitatively, 800 °C and 2—3 g of catalyst are suitable.

Ammonium sulfate required no additional covering catalyst for conversion into ammonia, low temperatures (700 °C) being suitable. Oxidation by Fe_xO_y produced on Al_2O_3 during pyrolysis supposedly causes NH_4^+ being partly converted into NO_x or N_2. A certain amount of $FeCl_3$ is necessary to release ammonia from the ammonium sulfate, since the recovery of ammonia was very low (55.1%) with use of only Al_2O_3, supporting no $FeCl_3$, as a catalyst at 800 °C.

Urea, containing one carbon atom in the molecule, requires higher temperatures for its conversion into ammonia as compared with ammonium sulfate, decreasing tendency in the recovery with an increase in the amount of catalyst being smaller than that of ammonium sulfate.

Effect of the Period of Time from Sample Insertion to Steam Supply. The method is not automatic, and sudden pyrolysis before the connection of the steam generator might cause a loss of some of the pyrolyzed products escaping out of the open end of the pyrolysis tube. A portion of the sample might burn, forming N_2 and NO_x instead of NH_3 as a result of the exposure to the air before steam is supplied.

The period of time from sample insertion to steam supply was varied using pyridine as a sample, and the effect on the recovery of nitrogen was investigated in order to estimate how long the period is allowed to determine nitrogen compounds quantitatively (Fig. 3). The concentration of $FeCl_3$ in the catalyst was 4%-Fe/Al_2O_3.

Although the boiling temperature of pyridine is

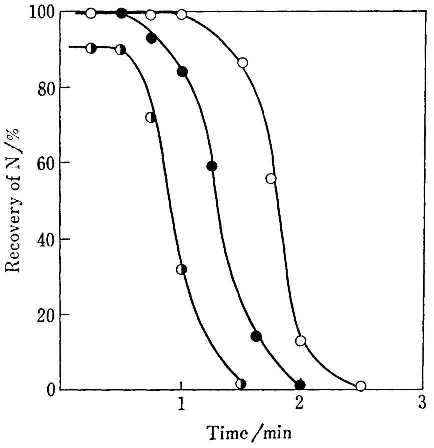

Fig. 3. Effect of the period of time from sample insertion to steam supply on the recovery of nitrogen. Reaction temperaure; ○: 800, ●: 900, ◑: 1000 °C, sample: pyridine (1 mg N), steam flow rate: 2.5 g/min.

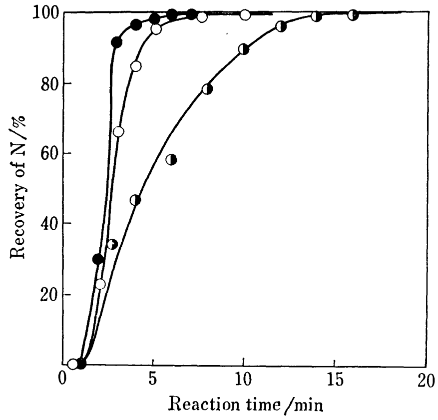

Fig. 4. Time required for pyrolysis reaction. Steam flow rate; ◑: 2.0, ○: 2.5, ●: 4.0 g/min, sample: pyridine (1 mg N), reaction temperature: 800 °C.

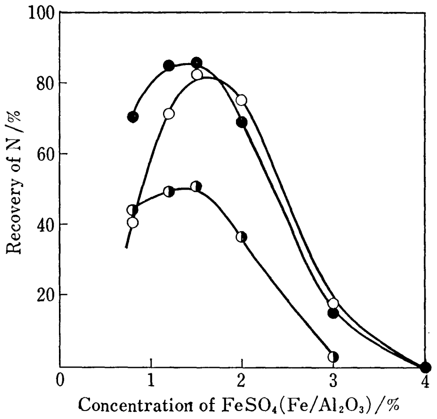

Fig. 5. Effect of $FeSO_4$ as a catalyst for pyrolysis. ○: Pyridine, ◑: *p*-dinitrobenzene, ●: azobenzene, reaction temperature: 800 °C, steam flow rate: 2.5 g/min.

Table 3. Application to various nitrogen compounds

Compound	Sample taken mg N	Found mg N
Pyridine	0.97	0.97
Quinoline	0.94	0.91
Acridine	1.01	0.98
Pyrrole	0.93	0.90
Indole	0.97	0.93
Carbazole	1.03	1.00
Aniline	1.00	0.97
Urea[a)]	1.00	0.98
Ammonium sulfate[a)]	1.00	1.00
N,*N*′-Diphenylthiourea	1.00	1.03
Phenazine	0.97	0.95
Imidazole	1.01	0.97
Acetanilide	0.98	0.95
p-Methoxybenzonitrile	0.97	0.95
p-Dinitrobenzene	1.00	0.76
5-Nitrosalicylic acid	0.99	0.89
Azobenzene	1.00	0.85
Benzotriazole	1.00	0.28

Reaction conditions; catalyst: 4%-Fe/Al_2O_3, reaction temp: 800 °C, steam: 2.5 g/min, reaction time: 10 min.
a) Covering catalyst: 0 g, reaction temp: 700 °C.

not high (115.5 °C), it was adsorbed on the catalyst in the hot zone of the pyrolysis tube at least for 1 min at 800 °C and 30 s at 900 °C presumably because of its adsorption to the catalyst and also the heat capacity of the sample boat and the catalyst, which prevent rapid rise in temperature.

Nitrogen in pyridine was not recovered quantitatively at 1000 °C, even when the steam was supplied immediately (5 s after insertion of the sample boat). Similar results were obtained in the case of aniline and indole. Thus, it is not necessary to connect the steam generator quickly.

Time Required for Pyrolysis. The effect of the steam flow rate on the pyrolysis of pyridine is shown in Fig. 4. The ammonia produced by the reaction at 800 °C was recovered quantitatively within 10 min at a flow rate higher than 2.5 g/min. As compared with other methods such as the conventional Kjeldahl and Dumas method, our method is simple and rapid, even though more time is requied for the steam distillation of ammonia as in the Kjeldahl method.

Other Materials as Catalysts for Pyrolysis. Iron(III) chloride supported on porous Al_2O_3 was found to be effective for the nitrogen determination of compounds of Type I. Iron(II) sulfate and $Fe(NO_3)_3$ were examined for the effect of anion on pyrolysis.

Plots of the concentration of $FeSO_4$ supported on Al_2O_3 (Fe/Al_2O_3) *vs.* the recovery of pyridine, *p*-dinitrobenzene, and azobenzene are given in Fig. 5. The recovery is not quantitative. As compared with chloride ion, highly concentrated sulfate ion adversely affects the pyrolysis of organic compounds.

The nitrate ion affected the reaction much more adversely, producing almost no ammonia but NO_x or N_2 releasing NO_2 due to the thermal decomposition of the nitrate ion.

Cobalt and nickel might also be useful for the reaction. However, $CoCl_2$ and $NiCl_2$ supported on Al_2O_3 gave no satisfactory results.

Application to Various Nitrogen Compounds. The results of various nitrogen compounds analyzed are given in Table 3. Compounds of Type I such as pyridine and aniline were determined satisfactorily, but not those of Types II and III, nitro and N–N bonded compounds.

Reproducibility of the Method. The reproducibility of the method was examined, the average recovery of pyridine ($n=8$) being 98.1% with a standard deviation of 0.77%.

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