Award Accounts

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Development of a New Production Process for *N*-Vinyl-2-pyrrolidone

Yuuji Shimasaki,*[1] Hitoshi Yano,[2] Hideto Sugiura,[3] and Hideyuki Kambe[4]

[1]Catalyst Research Center, Nippon Shokubai Co., Ltd., Aboshi-ku, Himeji 671-1292

[2]Process Technology Center, Nippon Shokubai Co., Ltd., Aboshi-ku, Himeji 671-1292

[3]Kawasaki Plant, Nippon Shokubai Co., Ltd., Kawasaki-ku, Kawasaki 210-0865

[4]Specialty Chemicals Business Unit, Nippon Shokubai Co., Ltd., Chuo-ku, Osaka 541-0043

Received June 29, 2007; E-mail: yuji_shimasaki@shokubai.co.jp

We describe the first continuous production process for *N*-vinyl-2-pyrrolidone (NVP). The starting materials are γ-butyrolactone (GBL) and monoethanolamine (MEA). The process consists of two stages: the synthesis of *N*-(2-hydroxyethyl)-2-pyrrolidone (HEP) from GBL and MEA, and the vapor-phase dehydration of HEP to NVP. The key features of this technology are the dehydration catalyst and the vapor-phase reaction system. The catalyst is of very simple composition, being alkali (or alkaline earth) metal oxides–SiO_2. Though its acid and base strengths are very weak, its catalytic performance is high. We presume that the excellent catalytic performance is due to the selective adsorption of HEP to the catalyst. Moreover, an IR spectroscopic study of the HEP-adsorbed catalyst indicated that the isolated silanol of the catalyst surface plays an important role. This account describes the progress made from the laboratory study to the industrial process, along with the experimental results and discussion.

1. Introduction

Since the 1980s, when people began to increasingly think about environmental problems due to growing concerns, the environment has been considered more and more in most global societal activities to enable realizing a sustainable society. This consideration has included the chemical industry, which has been required to design products and processes such that the processes do not consume large amounts of energy or produce large amounts of by-products.

Although continual efforts have been made in the chemical industry to improve production processes, some processes still consume large amounts of energy and raw materials and produce large amounts of waste. These processes should be replaced as soon as possible with environmentally friendly ones. One of the key means of designing an environmentally friendly process is catalytic technology, which can transform a stoichiometric reaction into a catalytic reaction. The use of catalysis can minimize the production of by-products, which are inevitable in a stoichiometric process. There are two types of catalytic reaction system: homogeneous and heterogeneous. Heterogeneous catalytic reaction systems are superior to homogeneous ones as green processes. The use of heterogeneous catalysts eases both the separation of the products from the catalyst and reuse of the catalyst. In particular, vapor-phase heterogeneous catalytic systems are advantageous because they can be operated in solvent free, continuous-flow systems. In contrast, in a homogeneous catalytic reaction system solvent is normally used and a continuous-flow system is difficult to employ. In addition, separation of the product from a reaction mixture is difficult, and the waste, which contains the catalyst, must be treated. Accordingly, the development of a vapor-phase heterogeneous catalytic system to replace a liquid-phase stoichiometric reaction system is desirable with respect to productivity and environmental concerns. An efficient vapor-phase production process is absolutely dependent on the development of an excellent catalyst. Many studies designed to improve the process and the catalyst have been done, both in academia and industry. Among various types of catalysts, acidic or basic metal oxide catalysts have been extensively studied. However, most of the catalysts studied have been solid acid catalysts or solid base catalysts. These promote the desired reactions, but their selectivity and catalytic life are often not practical for industrial use, probably because their active sites are too strong to work for long periods without deactivation. It should be possible to develop practical catalysts among those that possess both weakly acidic sites and weakly basic sites although there have been few studies of the development of bifunctional acid–base catalysts for industrial use.

We have been studying new production processes that use reactive monomers from hydroxyethyl compounds (derivatives of ethylene oxide) by vapor-phase dehydration. In 1991, we industrialized a new process for producing ethyleneimine by the vapor-phase dehydration of monoethanolamine (MEA) with an acid–base catalyst.[1] We later (1994) de-

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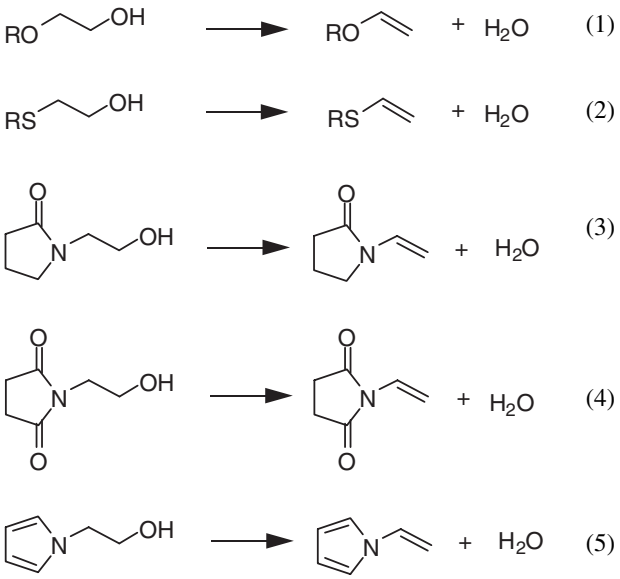
veloped excellent catalysts for the production of vinyl compounds from hydroxyethyl compounds by vapor-phase dehydration.

The catalysts' performance was high in the following dehydrations, which include dehydration of glycol ethers to vinyl ethers (eq 1),[2,3] dehydration of glycol thioethers to vinyl thioethers (eq 2),[4] dehydration of *N*-(2-hydroxyethyl)-cyclic amides to *N*-vinyl-cyclic amides (eq 3),[5] dehydration of *N*-(2-hydroxyethyl)-cyclic imides to *N*-vinyl-cyclic imides (eq 4),[6] and dehydration of *N*-(2-hydroxyethyl)-aromatic amines to *N*-vinyl-aromatic amines (eq 5).[7] R represents an alkyl group, an aryl group, or an aralkyl group in the eqs 1 and 2.

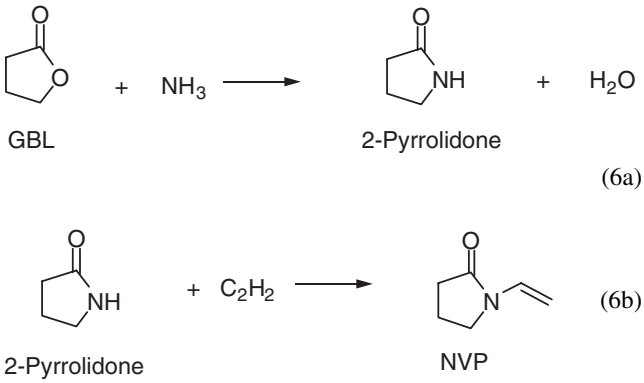


We found that SiO_2, modified by the addition of an alkali (or alkaline earth) metal oxide, exhibited high catalytic performance in the vapor-phase dehydration of hydroxyethyl compounds to the corresponding vinyl compounds. The newly developed catalysts produced vinyl ethers, vinyl thioethers, *N*-vinyl lactams, *N*-vinyl cyclic imides, and *N*-vinyl aromatic amines with high yields. In particular, *N*-vinyl-2-pyrrolidone (NVP) was produced in very high yield.

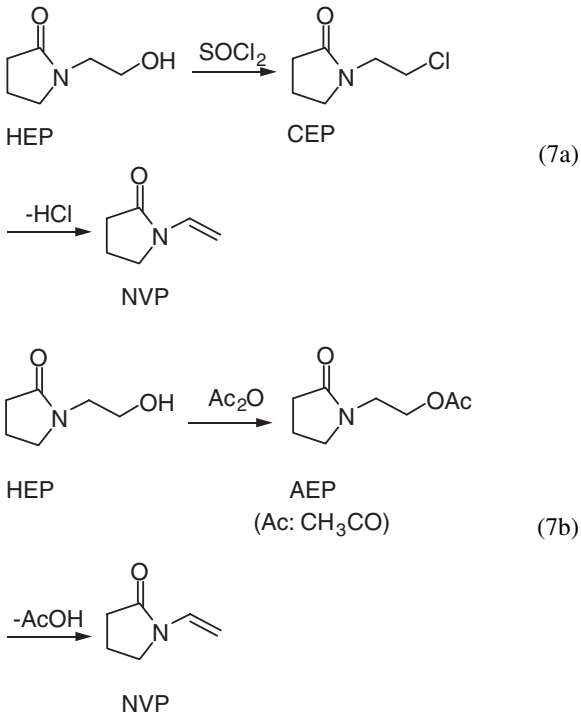
NVP, CAS [88-12-0], is a clear, colorless liquid that is miscible in all proportions with water and most organic solvents. The known properties of NVP are as follows:[8] mol wt. 111; boiling point at 53.3 kPa, 193 °C; freezing point, 13.5 °C; specific gravity (25/4 °C), 1.04.

NVP is a useful reactive monomer and is used principally for the production of homopolymers and copolymers. These polymers are used as the raw materials for pharmaceuticals, adhesives, paints, cosmetics, and many other chemical products.

NVP has been produced by the vinylation of 2-pyrrolidone, which is produced from γ-butyrolactone (GBL) and ammonia, with acetylene as the only industrial process (the Reppe process) since 1940 (eq 6).[9,10] This process presents some problems, such as the explosion risk of acetylene, necessary restriction of the plant location to sites close to acetylene production plants, and the exhaust of large amounts of alkaline waste and solvents.



Meanwhile, various processes using no acetylene have been disclosed that use HEP as a raw material, as follows:

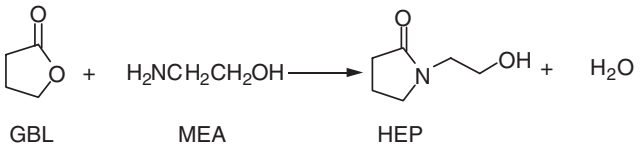


The process described in eq 7a is a dehydrochlorination of *N*-(2-chloroethyl)-2-pyrrolidone (CEP) obtained by the reaction of HEP with thionyl chloride.[11] The process described in eq 7b is an elimination of acetic acid from *N*-(2-acetoxyethyl)-2-pyrrolidone (AEP) obtained by the reaction of HEP with acetic anhydride.[12] These processes also present various problems: the sub-raw material is used in an amount equivalent to HEP, the cost of intermediate production is large, and by-products are generated from the sub-raw material in large amounts. Consequently, these processes are not well suited to industry.

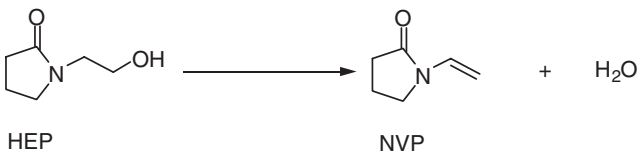
The above problems would be solved if the vapor-phase dehydration of HEP (eq 8a), which is produced from GBL and MEA, to NVP (eq 8b) were to efficiently proceed through the use of heterogeneous catalysts. Various oxides have been reported as the catalyst, including active alumina;[13] cerium oxide, zinc oxide, and chromium oxide;[14] zirconium oxide and thorium oxide;[15] lanthanum oxide and neodymium oxide;[16] acidic heterogeneous catalysts other than the oxides of metals

of group 12, 13, 14, and 16;[17] a mixed oxide of group 4 and 14 elements, or an oxide of group 4 and 14 elements that has been modified by group 1 or group 2 elements.[18]

Among them, zirconium oxide showed the highest catalytic performance (HEP conversion = 88.6%, NVP selectivity = 92.6%) in the patent.[15] However, in the experiment conducted by the authors using zirconium oxide under the reaction conditions of the present study, the conversion of HEP was as high as 84.9% but the selectivity of transformation to NVP, at 67.3%, was not sufficiently high to be used for a commercial process (eqs 8a and 8b).



(8a)



(8b)

We looked for catalysts that perform better than ZrO_2, and found that SiO_2 modified by the addition of alkali (or alkaline earth) metal oxides exhibits higher catalytic activity and selectivity.[19–21]

No industrial processes for the production of HEP existed until this new process to produce NVP was developed because HEP had no particular use. However, demand for HEP has increased, and the development of a process to produce it has become important. We investigated the reaction conditions in detail for the purpose of developing an industrial process for HEP production, and succeeded in developing a continuous-flow production system for HEP.

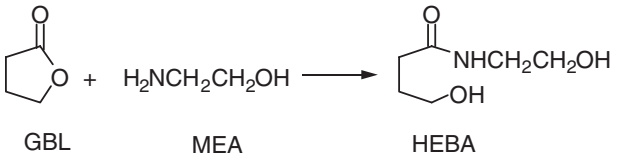
We also studied the purification of NVP and HEP, as well as the development of catalysts, and successfully tested the total process in the pilot plant. Based on these studies, our new commercial process for NVP synthesis was initiated at Nippon Shokubai's Kawasaki plant in 2001.

2. Development of a Continuous-Flow HEP Production System

A patent disclosed that HEP can be produced from GBL and MEA, and that the HEP yield is improved by the addition of water to the reaction system beforehand.[22] However, no example of a continuous-flow reaction was given, as all the examples in the patent were done batchwise. Also not reported was the purification process for HEP.

The preference was to use a continuous-flow system for the reaction and purification of HEP because we used such a system for the vapor-phase dehydration and purification of NVP. Hence, we developed a total continuous-flow process, from the introduction of starting materials to the storage of NVP.

The reaction of GBL and MEA conversion to HEP is shown in eq 8a. This reaction comprises two successive reactions (eq 9). The first reaction is the formation of *N*-(2-hydroxyethyl)-4-hydroxybutanamide (HEBA) from GBL and MEA, and the second reaction is the formation of HEP by the intramolecular dehydration of HEBA.



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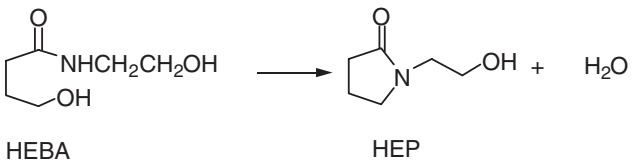


(9b)

2.1 Synthesis of HEBA from GBL and MEA (the First Reaction). The equivalents of GBL and MEA were put into a glass flask (capacity 50 mL) and stirred at 100 °C for 4 h. The products were analyzed by gas chromatography.

The conversion of MEA and the selectivity to HEBA based on MEA were defined as follows: conversion (mol %) = 100 × (mole of consumed MEA)/(mole of fed MEA); selectivity (mol %) = 100 × (mole of produced HEBA)/(mole of consumed MEA). The conversion of GBL and the selectivity to HEBA based on GBL were defined as follows: conversion (mol %) = 100 × (mole of consumed GBL)/(mole of fed GBL); selectivity (mol %) = 100 × (mole of produced HEBA)/(mole of consumed GBL).

Table 1 shows the effect of water on the conversion of MEA and the selectivities to HEBA in the first reaction. The reaction temperature was initially 25 °C and rose to 92 °C due to the heat of reaction. The MEA was completely consumed in 4 h. Water did not influence this reaction.

Figure 1 shows the relationship between the conversion of MEA and the reaction time in the presence of excess GBL (GBL/MEA = 39.0, molar ratio). The conversion of MEA increased with the reaction time and then reached saturation.

Figure 2 shows the relationship between the conversion of GBL and the reaction time in the presence of excess MEA (MEA/GBL = 38.3, molar ratio). In this case, the reaction was very fast, in contrast to that depicted in Figure 1. The conversion of GBL reached an upper limit in 10 min.

We think the reaction rate is faster under this condition because this reaction involves a nucleophilic attack by MEA on GBL. We tested the gradual addition of GBL to MEA in

Table 1. Effect of Water on the 1st Reaction[a)]

Time /h	H_2O /wt %	MEA Conv. /mol %	HEBA Sel. /mol %
0.5		84	100
4.0		100	100
0.5	10	84	100
4.0	10	100	100

a) Reaction conditions: MEA/GBL = 1/1 (molar ratio); temperature, 25 °C.

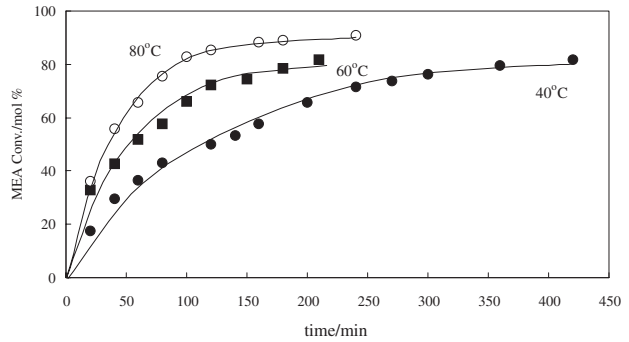


Figure 1. Relationship between the conversion of MEA and the reaction time in the presence of excess GBL. Reaction condition: GBL/MEA = 39.0, molar ratio.

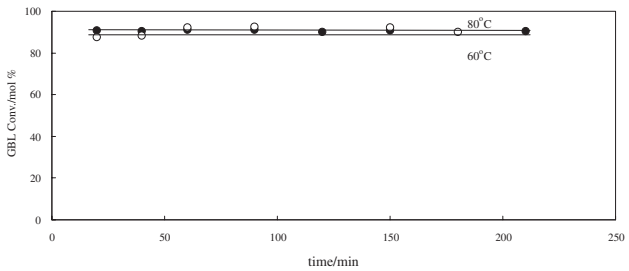


Figure 2. Relationship between the conversion of GBL and the reaction time in the presence of the excess MEA. Reaction condition: MEA/GBL = 38.3, molar ratio.

bench-scale experiments (described in Section **2.4**) in the expectation that it would have advantages as a practical method.

2.2 Synthesis of HEP from HEBA (the Second Reaction). HEBA was placed in a stainless steel reaction vessel and heated. The reaction was carried out in the temperature range of 200–250 °C. The products were analyzed by gas chromatography.

The conversion of HEBA and the selectivity to HEP were defined as follows: conversion (mol %) = 100 × (mole of consumed HEBA)/(mole of fed HEBA); selectivity (mol %) = 100 × (mole of produced HEP)/(mole of consumed HEBA).

Table 2 shows the effect of water on the second reaction. The addition of water dramatically increased the selectivity to HEP. The principal by-product was the condensed product of HEBA.

More detailed effects of temperature and water were examined by use of a 100-mL autoclave, as shown in Table 3. The effect of temperature was small. The amount of water influenced the selectivity to HEP. The addition of a large amount of water increased the selectivity to HEP, but lessened the productivity because it increased the load on the purification system.

The side reaction is the condensation of HEBA to form a by-product, as shown in eq 10. Water probably suppresses this side reaction. This condensation is presumably an equilibrium reaction, but the reaction of HEBA to HEP is not an equilibrium reaction. Thus, the condensation product (polymer) is converted back to HEBA by water, and is then converted to HEP.

Table 2. Effect of Water on the Second Reaction[a)]

H_2O /wt %	HEBA Conv. /mol %	HEP Sel. /mol %
0	96.2	82.8
10	98.4	90.2
50	99.8	92.9

a) Reaction conditions: reactor; 25-mL vessel, temperature; 250 °C, time; 1 h.

Table 3. Effect of Temperature in the Presence of Water on the Second Reaction[a)]

Temperature /°C	H_2O /wt %	Max. pressure /MPa	HEBA Conv. /mol %	HEP Sel. /mol %
250	10	1.6	93.7	90.1
270	10	2.1	94.7	91.1
250	30	2.5	93.1	93.9

a) Reaction conditions: reactor, 100-mL autoclave; temperature, 250 °C; time, 1 h.

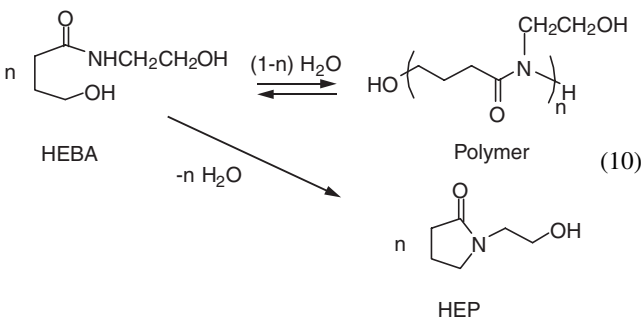
Table 4. Effect of MEA on the Second Reaction

HEBA/MEA (molar ratio)	Temperature /°C	Time /h	HEBA Conv. /mol %	HEP Sel. /mol %
HEBA only	250	3	100	87
10/5	250	3	100	97

Table 5. Comparison of the Reaction Method[a)]

Reaction method	Max. pressure /MPa	H_2O /wt %	HEBA Conv. /mol %	HEP Sel. /mol %
1-step reaction	1.9	10	100	88
2-step reaction	1.6	10	100	84

a) Reaction conditions: MEA/GBL = 1, molar ratio; reactor, 100-mL autoclave; temperature, 250 °C; time, 1 h.



(10)

Table 4 shows the effect of MEA on the second reaction. MEA did not inhibit the second reaction. MEA increased the selectivity to HEP as well as water did. It is likely that MEA acts as a base to promote the hydrolysis of the condensation product by the produced water.

2.3 One-Step Reaction. A one-step reaction was carried out by heating the crude product of the first reaction without the isolation of HEBA, as shown in Table 5. The selectivity to HEP was higher than that observed in the two-step reaction method. We consider this to be due to the effect of co-existing MEA because the second reaction proceeds in the presence of

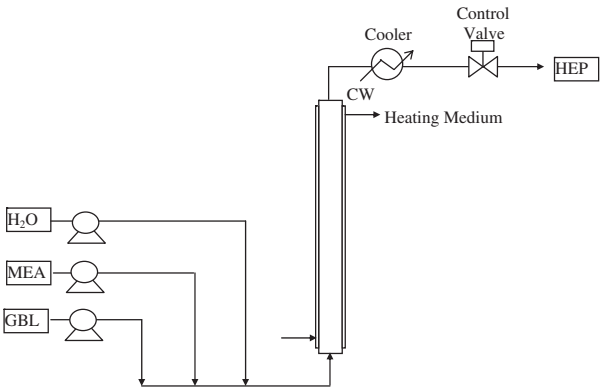


Figure 3. Model flow sheet of the new process of HEP production.

Table 6. Results of the Continuous-Flow Reaction[a)]

Temperature /°C	Back pressure /MPa	Residence time /h	MEA Conv. /mol %	HEP Sel. /mol %
250	3.7	0.99	100	89.3
		1.08	100	90.5
		1.3	100	91.6
		1.76	100	93.4
		2.8	100	93.2
260	4.1	1.08	100	92.0
		1.38	100	93.8
		1.71	100	93.9

a) Reaction conditions: GBL/MEA/H_2O = 1/1/1 (molar ratio); temperature, 250 °C.

the unreacted MEA in the two-step reaction.

2.4 Bench-Scale Production. Bench-scale production was carried out by use of a stainless steel reactor (capacity 100 L). An equivalent of GBL was added dropwise to MEA for 2.8 h without heating. The temperature increased as the reaction proceeded. The maximum reaction temperature was 76 °C. Next, water (30 wt %) was added to the reactor and stirred for 1 h at 250 °C. The reaction proceeded smoothly to completion, with no unusual elevation of temperature. The maximum pressure was 2.4 MPa. The conversion of MEA was 100%, and the selectivity to HEP was 94%.

2.5 Continuous-Flow Reaction. The continuous-flow reaction was carried out using the apparatus shown in Figure 3. The reactor was a stainless steel tube with an inside diameter of 16.2 mm and a length of 500 cm with structured packing inside. GBL, MEA, and water were fed into the reactor, and this mixture then passed through the reactor with a residence time of 0.99–2.8 h. The reactor was heated to the reaction temperature by use of a heating medium. Table 6 and Figure 4 show the results of the reaction.

The MEA conversion and the HEP selectivity values were very similar to those of the bench-scale production. The selectivity to HEP increased with the residence time. Raising the temperature shortened the residence time required to attain the upper limit of the yield of HEP, as shown in Figure 4. The continuous-flow reaction probably yielded the same result as the bench-scale reaction because high temperature does not inhibit the first reaction.

2.6 HEP Production: Conclusions. First, water does not influence the synthesis of HEBA from GBL and MEA (first reaction). Second, the first reaction reaches completion in a shorter time when GBL is gradually added to MEA. Third, the addition of water increases the selectivity to HEP dramatically in the synthesis of HEP from HEBA (second reaction). Fourth, water probably suppresses the side reaction (condensation of HEBA). Fifth, the one-step reaction method, which combines the first and the second reactions, is more productive for HEP synthesis. Sixth, we have developed a productive method for HEP production by use of a continuous-flow reaction system.[23]

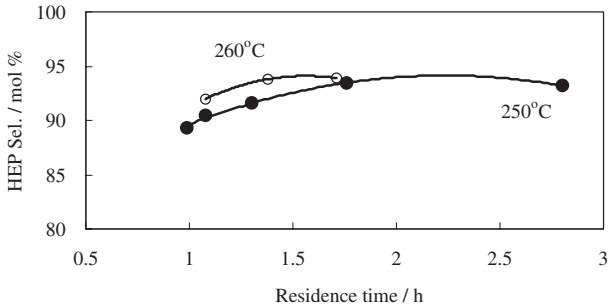


Figure 4. Selectivity to HEP vs. the residence time. Reaction conditions: GBL/MEA/H_2O = 1/1/1 (molar ratio); temperature, 250 °C.

3. Development of a Process for Vapor-Phase Dehydration HEP to NVP

3.1 Preparation of the Catalysts for Laboratory Experiments. To be of practical use, a catalyst must be physically strong enough to withstand the stresses it experiences within a reactor, for example, during moving and loading. Hence, industrial catalysts are made in various shapes, such as cylinders, tubes, and beads. They are shaped by molding, impregnation, or coating on a support. Molding usually reduces catalytic performance because the molding force changes properties of the catalyst, such as its pore size, pore volume, and density. To avoid these changes, additives that control the catalyst's physical properties and improve its strength are used. Our industrial catalyst was molded with careful consideration of the additive and molding conditions.

However, the catalysts for laboratory experiments were prepared by a simple method as follows.

3.1.1 Mono-Metal Oxide Catalysts: Silicon oxide (Sylysia 350, Fuji Silysia Chemical Ltd.) and ZrO_2 (Tokyo Chemical Industry Co., Ltd.) were used as starting materials. These oxides in powder form were first kneaded with water to form slurries. The slurries were dried at 120 °C for 20 h to form solids. The obtained solids were crushed into particles of 9–16 mesh and calcined at 500 °C for 2 h in air.

3.1.2 Metal Oxide Catalysts Modified with Alkali or Alkaline-Earth Metal Oxide: A mixture containing various metal oxides and hydroxides (or carbonates) of alkali or alkaline earth metals were kneaded with water. Each mixed oxide catalysts was prepared in a manner similar to the mono-metal oxide catalysts described above. All metal oxides (TiO_2, La_2O_3, and WO_3) were purchased from Tokyo Chemical Industry Co., Ltd.

3.2 Reaction Procedures. The vapor-phase dehydration

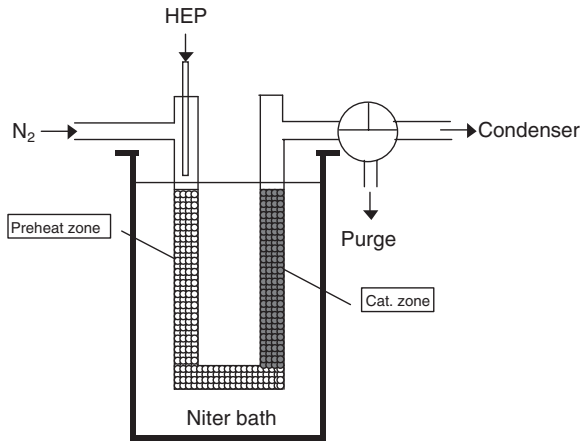


Figure 5. Laboratory-scale experimental equipment.

Table 7. Conversion and Selectivity in HEP Dehydration on Various Metal Oxides[a)]

Catalyst (molar ratio)	Reaction temp /°C	HEP conversion /mol %	NVP selectivity /mol %
SiO_2	400	16.3	94.2
Na_2O/SiO_2 (1/20)	370	57.0	98.7
ZrO_2	370	84.9	67.3
Na_2O/ZrO_2 (1/20)	370	97.3	23.6
Cs_2O/ZrO_2 (1/20)	350	98.8	20.5
Na_2O/TiO_2 (1/20)	370	13.2	44.2
Cs_2O/TiO_2 (1/20)	370	82.4	12.7
CaO/TiO_2 (1/10)	370	40.4	82.1
BaO/TiO_2 (1/10)	370	18.5	76.4
Na_2O/La_2O_3 (1/10)	370	19.7	61.9
Cs_2O/La_2O_3 (1/10)	350	69.8	9.2
Na_2O/WO_3 (1/20)	380	5.0	75.0
Cs_2O/WO_3 (1/20)	380	9.2	71.8

a) Reaction conditions: HEP gas concentration, 10 vol % (balanced by N_2); GHSV, 2000 h^{-1}; catalyst, calcined at 500 °C for 2 h.

was carried out in a fixed-bed flow-type reactor under atmospheric pressure.

Laboratory-scale experimental equipment is shown in Figure 5. Crushed catalysts (9–16 mesh, 5 cm^3) were placed in a stainless-steel reaction tube having an inside diameter of 10 mm, and heated to the reaction temperature in a molten-salt bath. The reactant gas of 10 vol % HEP in nitrogen was passed through the catalyst bed at a gas hourly space velocity (GHSV) of 2000–6000 h^{-1}. The reaction was carried out at 350–400 °C. After the reactant gas was fed for 1 h, the products were analyzed by gas chromatography.

3.3 Catalytic Performance of Various Metal Oxides. Table 7 shows the conversions of HEP and the selectivities to NVP in the presence of the metal oxides and various metal oxides loaded with alkali or alkaline earth oxides in the vapor-phase dehydration of HEP. The conversion of HEP and the selectivity to NVP were defined as follows: conversion (mol %) = 100 × (mole of consumed HEP)/(mole of fed HEP); selectivity (mol %) = 100 × (mole of produced NVP)/(mole of consumed HEP).

All the catalysts studied yielded NVP, though the conversion and selectivity changed depending on the type of catalyst (Table 7). Among them, both SiO_2 itself and modified SiO_2 catalysts showed greater than 90% selectivity to NVP. The major by-products observed were 2-pyrrolidone and acetaldehyde.

Table 8. Catalytic Performance of Alkali or Alkaline Earth Metal Oxide-Added SiO_2 Catalysts[a)]

Catalyst (molar ratio)	Reaction temp /°C	HEP conversion /mol %	NVP selectivity /mol %
SiO_2	400	16.3	94.2
Li_2O/SiO_2 (1/20)	400	59.2	99.2
Na_2O/SiO_2 (1/20)	370	57.0	98.7
K_2O/SiO_2 (1/20)	370	85.9	95.1
Rb_2O/SiO_2 (1/20)	370	89.8	94.2
Cs_2O/SiO_2 (1/20)	370	96.5	88.8
CaO/SiO_2 (1/10)	400	51.1	85.2
SrO/SiO_2 (1/10)	400	58.9	89.2
BaO/SiO_2 (1/10)	400	50.8	99.8

a) Reaction conditions: HEP gas concentration, 10 vol % (balanced by N_2); GHSV, 2000 h^{-1}; catalyst, calcined at 500 °C for 2 h.

With the SiO_2 catalyst itself, the selectivity to NVP was very high, while the conversion of HEP was low. The conversion was improved by the addition of a small amount of Na_2O to the SiO_2. The conversion obtained with this catalyst, Na_2O/SiO_2 (molar ratio 1/20), was much higher than that with SiO_2 alone, despite its lower reaction temperature, and the selectivity to NVP was also improved by the addition of Na_2O. Addition of alkali or alkaline-earth metal oxides to the metal oxides other than SiO_2 did not result in good catalytic performance.

3.4 Catalytic Performance of SiO_2 Modified with Alkali or Alkaline-Earth Metal Oxide. Table 8 shows the catalytic performance of SiO_2 enhanced with various kinds of alkali (or alkaline earth) metal oxides. The conversion of HEP was markedly improved by the addition of any type of alkali or alkaline-earth metal oxide to SiO_2. In general, alkali metal oxides were more effective in improving the activity than alkaline earth metal oxides.

The relationship between the catalytic performance and the ionization potential of the added alkali metal elements is shown in Figure 6. The conversion of HEP decreased and the selectivity to NVP increased with the decrease in the ionization potential of the alkali metal elements. The basicity of a metal oxide becomes stronger as the ionization potential of the metal elements decreases. The strength of basicity of alkali metal oxides is estimated to be in the order $Cs_2O > Rb_2O > K_2O > Na_2O > Li_2O$. This order may also hold when they are supported on SiO_2. We suggest that Cs_2O/SiO_2 has the highest activity because it has the strongest basicity among the SiO_2–alkali metal oxide mixtures.

The low activities of the alkaline-earth metal oxide-added SiO_2 as compared to those of alkali metal oxide-added SiO_2 might be due to the weaker basicity of the former. However, it is not necessarily true that the stronger the basic sites, the higher the activity, as described later in Section **3.8.1** on the basis of indicator color changes.

3.5 Effect of the Cs_2O Content of the Cs_2O/SiO_2 Catalyst. The effects of the amount of Cs_2O in the Cs_2O/SiO_2 catalyst on the conversion of HEP and the selectivity to NVP are shown in Figure 7. The conversion increased steeply as the amount of added Cs_2O increased to a Cs_2O/SiO_2 molar ratio of 0.0025, where the conversion was almost saturated. The

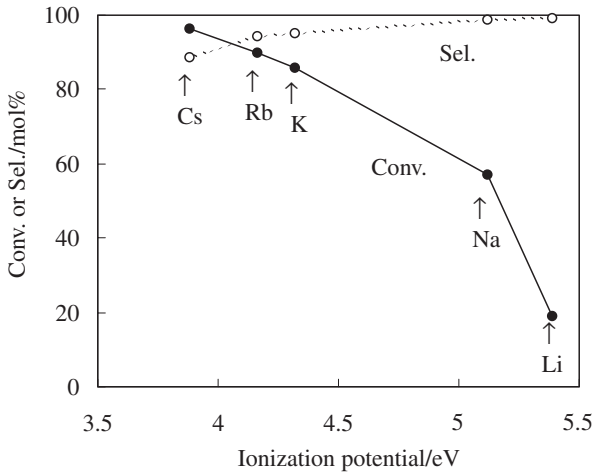


Figure 6. Relationships between ionization potential of alkali element added to SiO_2 and catalytic activity and selectivity. Reaction conditions: catalyst, alkali metal oxide/SiO_2 = 1/20 (molar ratio); HEP gas concentration, 10 vol% (balanced by N_2); GHSV, 2000 h^{-1}; reaction temperature, 370 °C; ionization potential: 5.39 eV/Li, 5.12 eV/Na, 4.32 eV/K, 4.16 eV/Rb, and 3.88 eV/Cs (Ref. 24).

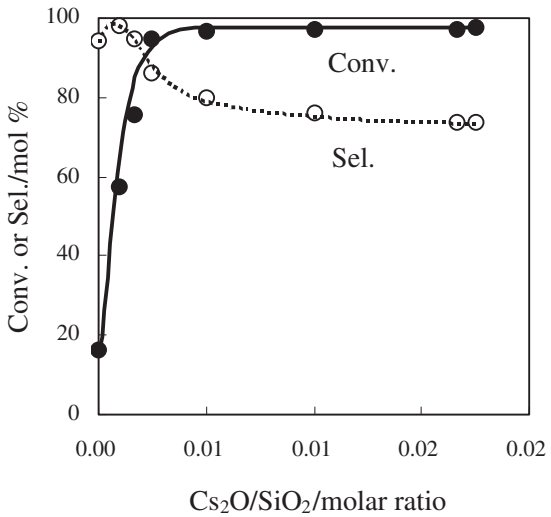


Figure 7. Effects of the amount of Cs in the Cs_2O/SiO_2 catalyst on the conversion and the selectivity. Reaction conditions: HEP gas concentration, 10 vol% (balanced by N_2); GHSV, 2000 h^{-1}; reaction temperature, 380 °C.

selectivity to NVP increased slightly with the addition of Cs_2O to a Cs_2O/SiO_2 molar ratio of 0.001, and gradually decreased with further increases in the amount of Cs_2O.

3.6 Effects of Reaction Conditions. Figure 8 shows the effects of GHSV and reaction temperature on the conversion of HEP in the presence of the catalyst Na_2O/SiO_2 (1/20 molar ratio) and a HEP concentration of 10 vol% in N_2. At 360 °C, the conversion increased linearly with the contact time, indicating that the reaction rate was 0 order with respect to HEP. As discussed later, the catalyst surfaces should be fully covered with HEP at this temperature, and little NVP remains on the surfaces. At 370 and 380 °C, however, the relationships

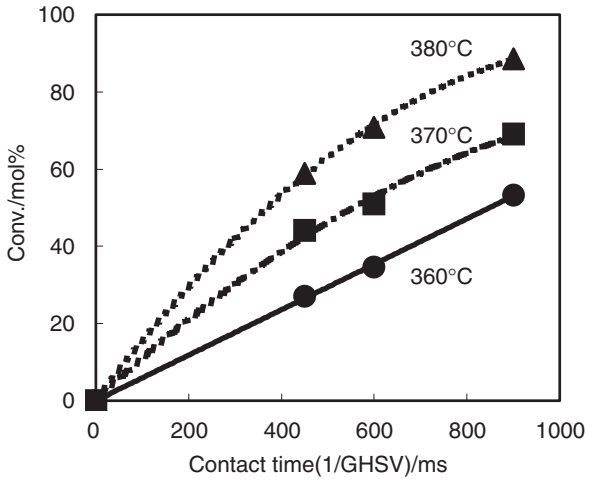
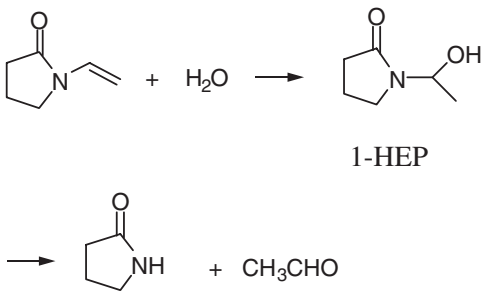


Figure 8. Variations of the conversion as a function of the contact time (1/GHSV) at different temperatures over the Na_2O/SiO_2 (1/20 molar ratio).

were not linear, indicating that the rates have positive-order kinetics with respect to HEP. The 0-order kinetics mean that only HEP was adsorbed to the catalyst. The positive-order kinetics mean that other reactants of HEP were also adsorbed to the catalyst. The amount of by-products acetaldehyde and 2-pyrrolidone increased at higher temperature. Equation 11 shows the side reaction. NVP is hydrolyzed to 2-pyrrolidone and acetaldehyde via *N*-(1-hydroxyethyl)-2-pyrrolidone (1-HEP). Using the pulse method, we observed that 2-pyrrolidone was adsorbed strongly to the catalyst. We believe that the positive-order kinetics are due to the adsorption of 2-pyrrolidone to the catalyst. Based on the initial rates at different temperatures, the activation energy is calculated to be 153.3 kJ mol^{-1}.



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3.7 The Change of Catalytic Performance with Time on Stream. Figure 9 shows our one example of a change in catalytic performance with time on stream. The conversion of HEP gradually decreased with time on stream. The cause of the decrease in conversion was coke deposition on the catalyst's surface. The conversion was recovered by the regeneration of the catalyst. Catalyst regeneration was carried out by heating at the reaction temperature in the presence of synthetic air. The degree of recovery attainable by regeneration is nearly steady with long time on stream. However, it eventually gradually decreases with very long continuous use. This deactivation is due to the sintering of the catalyst. The selectivity to NVP was almost constant with time on stream.

The industrial catalyst maintained steady performance for over 1 year, and 1 kg of the catalyst produced more than 15 tons of NVP per year.

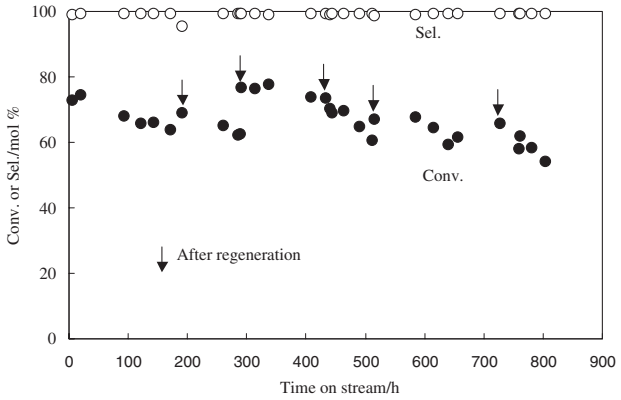

Figure 9. Change in catalytic performance with time on stream. Reaction conditions: catalyst, $Na_2O/P_2O_5/SiO_2$ = 5/1/100 (molar ratio), calcined at 600 °C for 3 h; HEP gas concentration, 10 vol % (balanced by N_2); GHSV, 4000 h^{-1}; reaction temperature, 380 °C.

3.8 Features of the Catalysts and the Reaction Mechanism. The properties of the catalyst were investigated through measurements of their acid and base strengths, the adsorption and desorption behaviors of some reactants on the catalyst, and the temperature-dependent IR spectra of the HEP-adsorbed catalyst. We applied the results to an analysis of the reaction mechanism.

3.8.1 Acid and Base Strengths of Catalysts: The acid and base strengths of the catalysts were measured by the indicator method.[25] The indicators used were *p*-dimethylaminoazobenzene ($pK_a = +3.3$), 4-phenylazo-1-naphthylamine ($pK_a = +4.0$), neutral red ($pK_a = +6.8$), bromothymol blue ($K_{BH} = +7.2$), phenolphthalein ($K_{BH} = +9.4$), and 2,4,6-trinitroaniline ($K_{BH} = +12.2$).

The maximum acid strength of SiO_2 itself was $H_0 = +3.3$. In contrast, the alkali metal oxide-added SiO_2 catalysts did not change the colors of all the indicators used; namely, the acid strength is weaker than $H_0 = +6.8$ and the base strength is weaker than $H_- = +7.2$. This result is reasonable because this catalyst can be considered to be the salt (cesium silicate) formed by the neutralization of CsOH and silicic acid. It is probable that these weak active sites are strong enough to effect the dehydration of HEP under high temperature.

3.8.2 Adsorption and Desorption Behaviors of Various Reactants: This experiment was performed using the pulse method as follows: the catalyst (Na_2O/SiO_2, 50 mg, 1/20 molar ratio), was fixed by quartz wool in the center of a stainless-steel reaction tube having an inside diameter of 4 mm and a length of 10 cm. Nitrogen gas was passed through the catalyst, which was kept at 300 °C. A constant quantity (0.3 μL) of the reactant was injected successively into the nitrogen stream ahead of the catalyst. The outlet gases were monitored by mass spectrometry. HEP, NVP, and *N*-ethyl-2-pyrrolidone (NEP) were used as the reactants. NEP was used to investigate the effect of the hydroxy group alone, since a hydroxy group in HEP is replaced by hydrogen in NEP.

As shown in Figure 10, the desorption peak intensity of HEP increased with the pulse number for the initial four pulses and then leveled off after the fifth pulse. Each HEP peak had a long tail, suggesting that HEP is strongly adsorbed to the catalyst. In contrast, the intensities of the desorption peaks of NEP corresponded to the injection amount regardless of the pulse number, and lacked long tails. These results indicate that NEP is not strongly adsorbed to the catalyst. During the reaction of HEP, the surface active sites are fully covered with HEP; NVP is desorbed immediately after it is formed by the dehydration of HEP. The adsorption behavior of NVP is similar to that of NEP, indicating that NVP is also adsorbed weakly to the catalyst. Considering the strong adsorption of HEP and weak adsorption of NEP, we suggest that the strong adsorption of HEP is due to the interaction of its OH group with the surface of the catalyst.

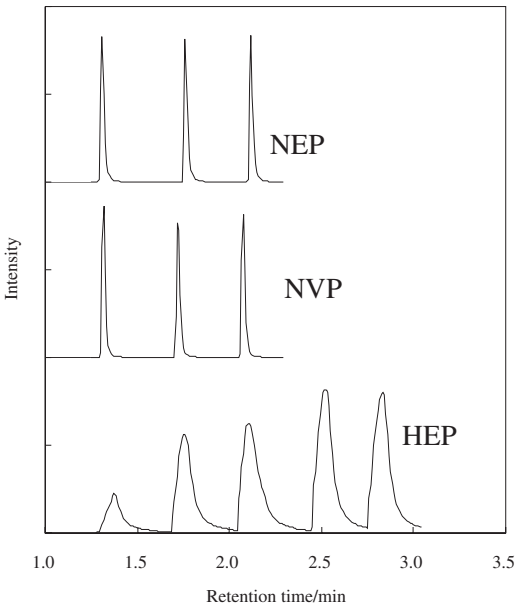

Figure 10. Desorption peaks of each reagent in the pulse adsorption method. *HEP peaks were magnified 5 times.

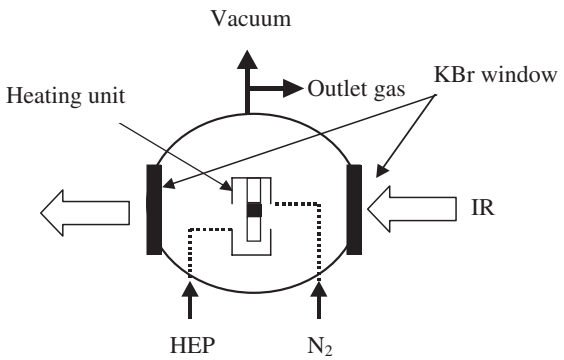

Figure 11. Variable temperature IR unit.

3.8.3 Variable-Temperature IR: The IR spectra were measured at different temperatures. The variable-temperature IR unit we used is shown in Figure 11.

The IR spectrum of the fresh catalyst, from which the adsorbents were desorbed at 400 °C under flowing N_2, shows the absorption peak of the single silanol at 3740 cm^{-1}. This peak was almost absent from the spectrum of the HEP-adsorbed catalyst, which was treated at 100 °C, as shown in Figure 12. This peak increased only slightly when the temperature was raised to 200 °C, demonstrating that some of the

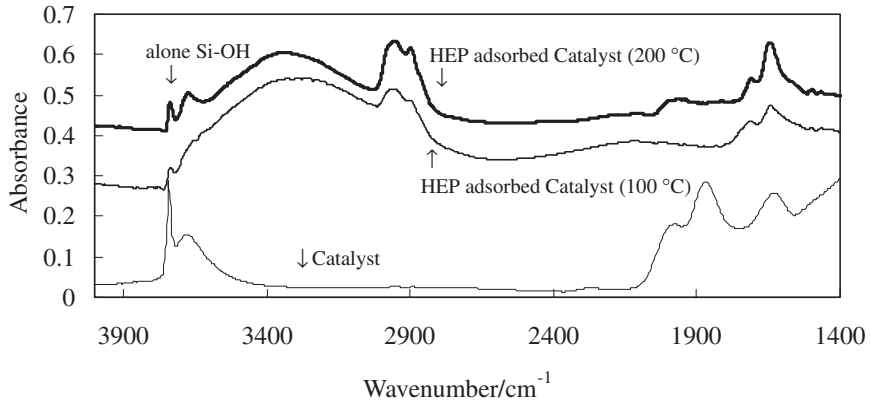

Figure 12. IR spectrum of the HEP-adsorbed catalyst. Catalyst: Cs_2O/SiO_2 (1/20 molar ratio), Calcined at 500 °C for 2 h.

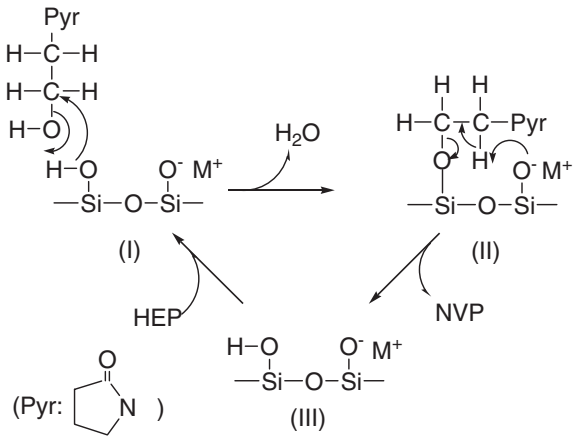

Figure 13. Reaction mechanism proposed for the dehydration of HEP to NVP.

HEP was converted to NVP and desorbed from the catalyst. This result suggests that HEP is adsorbed to the silanol group on the catalyst.

3.8.4 Reaction Mechanism: The adsorption of HEP and the successive reactions are proposed as shown in Figure 13. From the fact that this reaction occurred on SiO_2 alone, as seen in Table 7, it seems possible that the active sites are acidic and basic sites of the hydroxy group on SiO_2. This hydroxy group can remain on the alkali metal oxide/SiO_2 catalyst because the amount of alkali metal oxide is not large enough to cover the SiO_2 surface. The acidic sites presumably interact with the O atom of the OH group in HEP. HEP is first adsorbed to the silanol of the catalyst surface by the dehydration involving the OH group of HEP and silanol (I). The basic site, which is strengthened by the electron donation of Cs, pulls a proton from the α-carbon atom, and vinylation occurs (II).

The comparison of the catalytic performance of SiO_2 with that of SiO_2 enhanced with alkali or alkaline-earth metal oxide in Table 8 indicates that acidic catalysts have low activity while basic catalysts have much higher activity. The selectivity to NVP is almost unchanged, regardless of the activity. This tendency is not clear for the catalysts other than SiO_2. The acidic sites, proton of silanol and/or alkali metal cation of silicate, probably play an important role in determining catalytic performance.

3.9 Dehydration of HEP to NVP: Conclusions. First, SiO_2 to which a small amount of alkali metal oxide was added exhibited pronounced catalytic activity in the intramolecular dehydration of HEP to NVP in the vapor phase. Second, the conversion of HEP decreased and the selectivity to NVP increased with an increase in the ionization potential of the alkali metal element added to SiO_2. Third, for a catalyst to be efficient, the acid strength should be weaker than $H_0 = +6.8$ and the base strength weaker than $H_- = +7.2$. Fourth, it is presumed that HEP is adsorbed to acid–base pairs on the catalyst through the interaction of the hydroxy group in the molecule with those sites, forming NVP by intramolecular dehydration.

4. The Process of NVP Production from MEA and GBL

The total process consists of four parts: the HEP reaction system, the HEP purification system, the NVP reaction system, and the NVP purification system. A model flow sheet of the new process of NVP production is shown in Figure 14.

Each system was established through an escalation from a laboratory scale to a bench and a pilot scale process. We simultaneously developed the process for producing the practical catalyst.

Both higher quality and lower cost relative to other NVP syntheses currently in use were necessary for a foray into the market. Many factors were optimized, including influences on stability and the cost of storage, as well as differences in the new products' reaction behavior from that of the current NVP. Fortunately, the very high performance of the catalyst enabled the use of simple purification systems and attainment of the desired quality and cost.

4.1 Process of HEP Production. The reaction of GBL and MEA to form HEP is carried out in the HEP tube reactor, which contains structured packing. Water is simultaneously fed to the reactor. This reaction is controlled by the composition of the reactants, the residence time, and the temperature. HEP is purified by water stripping, removal of the heavy by-product, and recovery of the GBL. GBL is formed by the decomposition of the heavy by-product at the bottom of the HEP recovery column. Both GBL and water are recycled.

4.2 Process of NVP Production. The NVP production process consists of the vapor-phase reaction system, the trapping system, and the purification system.

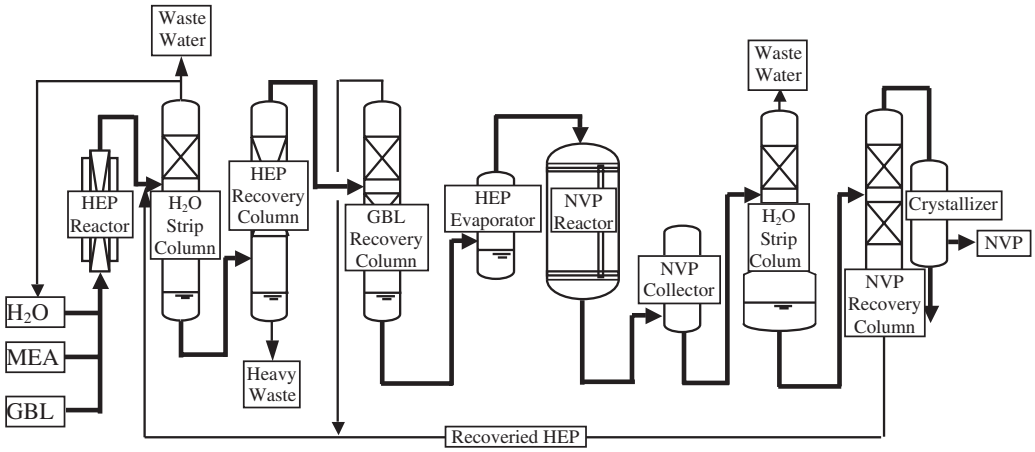

Figure 14. Model flow sheet of the new process of NVP production.

The vapor-phase reaction system is the core of this new NVP production process. In general, an inert carrier gas, such as nitrogen, is fed to a reactor to control the partial pressure of the raw material and to carry out a continuous vapor-phase catalytic reaction. It usually requires a large-scale absorption column as well as a large amount of solvent to condense the reaction products. Moreover, large volumes of inert carrier gas have to be treated for recycling. In the new process, HEP is fed to a fixed-bed-catalyst reactor equipped with a shell and tube heat exchanger, with no carrier gas, under reduced pressure. Consequently, the reaction products are easily condensed upon cooling, without any losses.

4.2.1 Vapor-Phase Reaction System: The following is a practical example. HEP was evaporated and fed to a reactor at a pressure of 10 kPa, a GHSV of 135–200 h^{-1}, and a reaction temperature of 360–380 °C. The selectivity of NVP was 98–99%, and the conversion of HEP was 85%. The by-products, aside from water, were small amounts of acetaldehyde and 2-pyrrolidone.

If the catalyst has carbon deposits, it can be reactivated quickly by aeration at the reaction temperature. As a result, the catalyst has a considerably long life and the reaction can be run stably for long periods.

4.3 NVP Purification System. The high selectivity of NVP in the vapor-phase dehydration allows us to produce highly pure NVP (above 99.9%), as it is easy to remove the water from the condensed reaction products by distillation and then separate the NVP from unreacted HEP by distillation. Unreacted raw material (HEP) can be recycled.

The distilled NVP contains small amounts of by-products. These impurities could cause problems in the polymerization of some kinds of polymers, so a further purification step, such as crystallization, is required to purify distilled NVP.

4.4 Features of the New Process. The new process can be operated continuously, from HEP production to NVP purification, by several operators. The production yield of the process is much higher than that of the conventional Reppe process. The process produces high-purity NVP with small amounts of wastes, which are composed mainly of water. It is thus the most environmentally friendly process for NVP production, overcoming the drawbacks of the Reppe process, and is particularly suitable for mass production.

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Yuuji Shimasaki was born in 1958 in Kochi, Japan. After graduating Tokyo University of Agriculture and Technology in 1980, he entered Graduate School of Nagoya Institute of Technology. After he received a master's degree from Nagoya Institute of Technology in 1982, he joined Nippon Shokubai Chemical Industry. He was engaged in studies on methacrylic acid synthesis catalyst during 1982–1984. After that he has been studied a solid acid–base catalysts and vapor-phase organic syntheses up to 2004. During that he wrestled with the development of ethyleneimine production process and catalyst from 1984 to 1990, and the development of *N*-vinyl-2-pyrrolidone production process and catalyst from 1991 to 2001. In 1992 he received the 41st Chemical Society of Japan Award for Technical Development, and the Catalyst Society of Japan Award in Technical Division. He has been a General Manager of Process Technology Center of Nippon Shokubai Co., Ltd during 2004–2007. Now, he is a General Manager of Catalyst Research Center of Nippon Shokubai Co., Ltd.

Hitoshi Yano was born in 1962 in Wakayama, Japan. After graduating Kyoto University of in 1984, he entered graduate school of the same university. After he received a master's degree from Kyoto University in 1986, he joined Nippon Shokubai Chemical Industry. He was engaged in the development of ethyleneimine production process and catalyst from 1986 to 1990, development of ethylene sulfide production process and catalyst from 1991 to 1995 and the development of *N*-vinyl-2-pyrrolidone production process and catalyst from 1995 to 2001. He is a General Manager of Process Technology Center of Nippon Shokubai Co., Ltd from April 2007.

Hideto Sugiura was born in 1972 in Kanazawa, Japan. After graduating School of Engineering, Nagoya University in 1995, he entered graduate school of same university. After he received a master's degree from Graduate School of Engineering, Nagoya University in 1997, he joined Nippon Shokubai Co., Ltd. He was engaged in remodeling of ethylene oxide process in Kawasaki Chidori Plant during 1997–1999. After that he has been designed *N*-vinyl-2-pyrrolidone production process up to 2006. During that he has been designed poly(vinylpyrrolidone) production process from 2003 to 2006. From 2006, he has been engaged in remodeling of ethylene oxide process in Kawasaki Ukishima Plant. Now, he belongs to Technology Department of Kawasaki Plant of Nippon Shokubai Co., Ltd.

Hideyuki Kambe was born in 1964 in Hyogo, Japan. After graduating Himeji Institute of Technology in 1987, he entered graduate school of Osaka university. After he received a master's degree from Osaka University in 1989, he joined Nippon Shokubai Chemical Industry. He was engaged in the studies of a solid acid–base catalysts and vapor-phase organic syntheses from 1989 to 2001. He devoted himself to the development of *N*-vinyl-2-pyrrolidone production process and catalyst during 1995–2001. Now, he is a Manager of Performance Chemical Business Division of Nippon Shokubai Co., Ltd.