

Vapor phase intramolecular dehydration of *N*-(2-hydroxyethyl)-2-pyrrolidone to *N*-vinyl-2-pyrrolidone over alkali metal oxide/SiO₂ catalysts

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Abstract

Silica catalysts modified with alkali metal oxide and alkaline earth metal oxide exhibited an excellent catalytic performance in the vapor phase intramolecular dehydration of *N*-(2-hydroxyethyl)-2-pyrrolidone to *N*-vinyl-2-pyrrolidone in the temperature range of 360–400 °C. The high activity and selectivity are considered to be due to the presence of both weak acid sites and weak basic sites on the modified SiO₂.

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1. Introduction

N-vinyl-2-pyrrolidone (NVP) is a useful reactive monomer, which is used principally for the production of homopolymers and copolymers. These polymers are used as raw materials for pharmaceuticals, adhesives, paints, cosmetics and many others.

The reaction of 2-pyrrolidone with acetylene in the presence of strong alkali in liquid phase is well known as a commercial process of NVP production (Scheme 1) [1]. This process, however, has some problems as follows:

- (i) It poses an explosion risk caused by the use of acetylene.
- (ii) The production facilities have to be located close to acetylene production plants.

- (iii) Alkaline salts of 2-pyrrolidone are used as the catalyst for acetylene addition reaction and the process exhausts a large amount of alkaline waste and solvents.

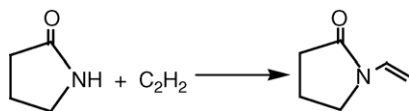
The above problems will be solved if the vapor phase intramolecular dehydration of *N*-(2-hydroxyethyl)-2-pyrrolidone (HEP) to NVP (Scheme 2) proceeds efficiently by using heterogeneous catalyst. Although the intramolecular dehydration is known to proceed over ZrO₂ catalyst [2], the catalytic activity of ZrO₂ is not sufficiently high to be used for a commercial process.

We have been searching for a catalyst better than ZrO₂, and found that SiO₂ turned out highly active and selective by addition of alkali metal oxides or alkaline earth metal oxides [3]. Based on this type of catalyst, our new NVP production process started up in the fourth quarter of 2001.

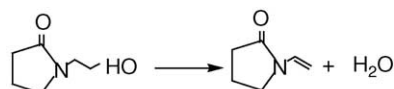
We wish to report the performance of the SiO₂ catalysts to which alkali or alkaline earth metal oxides were added, and the features of the active catalysts.

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Scheme 1. Formation of NVP from 2-pyrrolidone and acetylene.



Scheme 2. Intramolecular dehydration of HEP to NVP.

The practical catalyst was developed on the basis of this study.

2. Experimental

2.1. Preparation of catalysts

Metal oxides (SiO_2 and ZrO_2) and alkali (or alkaline earth) metal oxides (oxides of Li, Na, K, Rb, Cs, Ca, Sr and Ba) added metal oxides (SiO_2 , ZrO_2 , TiO_2 , La_2O_3 and WO_3) were studied as the catalysts in this work.

2.1.1. Metal oxide catalysts

Starting materials of SiO_2 and ZrO_2 were SYLISIA 350 (Fuji Silysia Chemical Ltd.) and ZrO_2 (Tokyo Chemical Industry Co., Ltd.), respectively. These oxides in the 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.

2.1.2. Alkali or alkaline earth metal oxide-added metal oxide catalysts

The mixtures containing various metal oxides and hydroxides (or carbonates) of alkali or alkaline earth oxides were kneaded with water. Then, the catalysts were prepared by the same manner as in the metal oxide catalysts described above. All metal oxides (TiO_2 , La_2O_3 and WO_3) were purchased from Tokyo Chemical Industry Co., Ltd.

2.2. Reaction procedures

The vapor phase dehydration was carried out in a fixed bed flow type reactor under atmospheric pressure. Pulverized catalyst (9–16 mesh, 5 cm^3) was placed in the 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. Reaction was carried out in the temperature range of 350 – 400°C . The products were analyzed by gas chromatography.

2.3. Measurement of acid and base strengths of catalysts

Acid and base strengths of the catalysts were measured by the indicator method [4]. Indicators used were *p*-dimethylaminoazobenzene ($\text{p}K_{\text{a}} = +3.3$), 4-phenylazo-1-naphthylamine ($\text{p}K_{\text{a}} = +4.0$), neutral red ($\text{p}K_{\text{a}} = +6.8$), phenolphthalein ($K_{\text{BH}} = +9.4$) and 2,4,6-trinitroaniline ($K_{\text{BH}} = +12.2$).

2.4. Adsorption and desorption behavior of reactants on catalyst

The catalyst (50 mg) was fixed by quartz wool in the center of a stainless steel-made reaction tube having an inside diameter of 4 mm and a length of 10 cm. The nitrogen gas was passed through the catalyst kept at 300°C . A constant quantity ($0.3\ \mu\text{l}$) of the reagent was injected successively into the nitrogen stream ahead of the catalyst. The outlet gases were monitored by mass spectrometry.

3. Results and discussion

3.1. Catalytic performance of various metal oxides

Table 1 shows the conversions of HEP and the selectivities to NVP over the metal oxides and various metal oxides loaded with alkali or alkaline earth oxide in the vapor phase dehydration of HEP. The conversion of HEP and the selectivity to NVP are defined as follows in the present report.

Conversion (mol%) = $100 \times (\text{mol of consumed HEP}) / (\text{mol of fed HEP})$;

Selectivity (mol%) = $100 \times (\text{mol of produced NVP}) / (\text{mol of consumed HEP})$.

As shown in Table 1, all of the catalysts studied yielded NVP though the conversion and selectivity depended on the

Table 1
Conversion and selectivity in HEP dehydration on various metal oxides

Catalyst (molar ratio)	Reaction temperature ($^\circ\text{C}$)	HEP conversion (mol%)	NVP selectivity (mol%)
SiO_2	400	16.3	94.2
$\text{Na}_2\text{O}/\text{SiO}_2$ (1/20)	370	57.0	98.7
ZrO_2	370	84.9	67.3
$\text{Na}_2\text{O}/\text{ZrO}_2$ (1/20)	370	97.3	23.6
$\text{Cs}_2\text{O}/\text{ZrO}_2$ (1/20)	350	98.8	20.5
$\text{Na}_2\text{O}/\text{TiO}_2$ (1/20)	370	13.2	44.2
$\text{Cs}_2\text{O}/\text{TiO}_2$ (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
$\text{Na}_2\text{O}/\text{La}_2\text{O}_3$ (1/10)	370	19.7	61.9
$\text{Cs}_2\text{O}/\text{La}_2\text{O}_3$ (1/10)	350	69.8	9.2
$\text{Na}_2\text{O}/\text{WO}_3$ (1/20)	380	5.0	75.0
$\text{Cs}_2\text{O}/\text{WO}_3$ (1/20)	380	9.2	71.8

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

Table 2
Catalytic performances of alkali or alkaline earth metal oxide-added SiO₂ catalysts

Catalyst (molar ratio)	Reaction temperature (°C)	HEP conversion (mol%)	NVP selectivity (mol%)
SiO ₂	400	16.3	94.2
Li ₂ O/SiO ₂ (1/20)	400	59.2	99.2
Na ₂ O/SiO ₂ (1/20)	370	57.0	98.7
K ₂ O/SiO ₂ (1/20)	370	85.9	95.1
Rb ₂ O/SiO ₂ (1/20)	370	89.8	94.2
Cs ₂ O/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

Reaction conditions: HEP gas concentration: 10 vol% (balanced by N₂). GHSV: 2000/h; catalyst: calcined at 500 °C for 2 h.

types of catalyst. Among them, SiO₂ catalysts, both modified and non-modified, showed the NVP selectivity higher than 90%. The principal by-products observed were 2-pyrrolidone and acetaldehyde.

With SiO₂ catalyst itself, the NVP selectivity was very high while the HEP conversion was low. Such a low conversion was improved by the addition of a small amount of Na₂O to SiO₂. The conversion obtained with this catalyst (Na₂O/SiO₂ (1/20)) was much higher than that with SiO₂ alone in spite of lower reaction temperature, and the NVP selectivity was also improved by the addition of Na₂O.

Addition of alkali or alkaline earth metal oxides to the metal oxides other than SiO₂ did not result in a good catalytic performance.

3.2. Catalytic performance of alkali or alkaline earth metal oxide-added SiO₂

Table 2 shows catalytic performance of various kinds of alkali (or alkaline earth) oxide-added SiO₂. The HEP conversion was markedly improved by the addition of any type of alkali or alkaline earth metal oxides to SiO₂. In general, alkali metal oxides were more effective in improving the activity than alkaline earth oxides.

The relationship between the catalytic performance and the ionization potential of the added alkali elements is shown in Fig. 1. The HEP conversion decreased and the NVP selectivity increased with the decrease in the ionization potential of alkali elements. The basicity of metal oxide becomes stronger as the ionization potential of the metal is lower. The strength of basicity of alkali metal oxides is estimated to be in the order: Cs₂O > Rb₂O > K₂O > Li₂O. The order may hold when supported on SiO₂. The highest activity of Cs₂O/SiO₂ is suggested to be due to the strongest basicity among alkali metal oxide-added SiO₂. The low activities of alkaline earth oxide-added SiO₂ as compared to those of alkali metal oxide-added SiO₂ may be due to the weaker basicity for the former than the latter. However, it is not necessarily true that the stronger the basic sites, the higher the activity as described later in

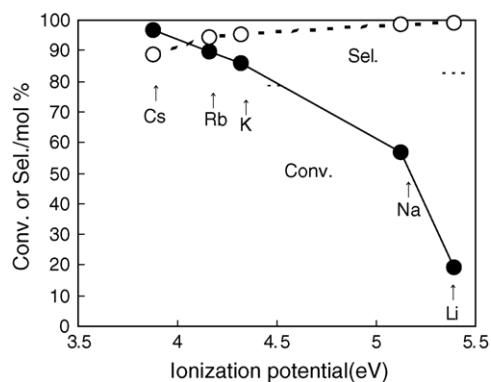


Fig. 1. Relationships between ionization potential of alkali element added to SiO₂ and catalytic activity and selectivity. Reaction conditions: catalyst, alkali metal oxide/SiO₂ = 1/20 (molar ratio); HEP gas concentration, 10 vol% (balanced by N₂); GHSV, 2000/h; reaction temperature, 370 °C. Ionization potential: 5.39 eV/Li, 5.12 eV/Na, 4.32 eV/K, 4.16 eV/Rb and 3.88 eV/Cs [5].

Section 3.4 on the basis of observation of color change of the indicators.

3.3. Effect of the amount of Cs in Cs₂O/SiO₂ catalyst

The effects of the amount of Cs in Cs₂O/SiO₂ catalyst on the conversion of HEP and the selectivity to NVP are shown in Fig. 2. The conversion increased steeply as the amount of Cs added increased to 0.05 atomic ratio of Cs/Si where the conversion almost saturated. The selectivity slightly increased on addition of Cs in the Cs/Si ratio of 0.002, and gradually decreased with further increase in the amount of Cs.

3.4. Acid and base strengths of catalysts

The maximum acid strength of SiO₂ itself was $H_0 = +3.3$. On the other hand, the alkali metal oxide-added SiO₂ catalysts

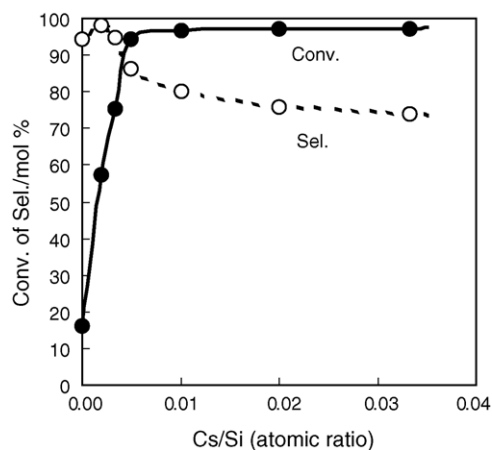


Fig. 2. Effects of the amount of Cs in Cs₂O/SiO₂ catalyst on the conversion and selectivity. Reaction conditions: HEP gas concentration, 10 vol% (balanced by N₂); GHSV, 2000/h; reaction temperature, 380 °C.

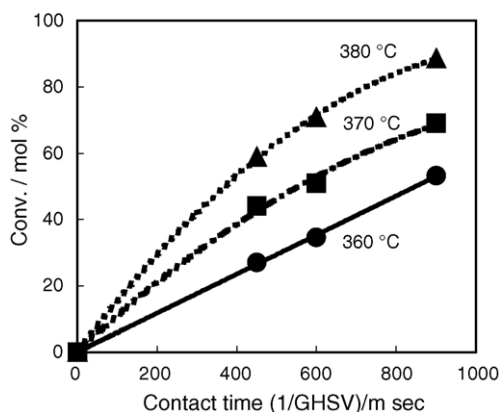


Fig. 3. Variations of the conversion as a function of the contact time (GHSV)⁻¹ at different temperatures over Na₂O/SiO₂ (1/20).

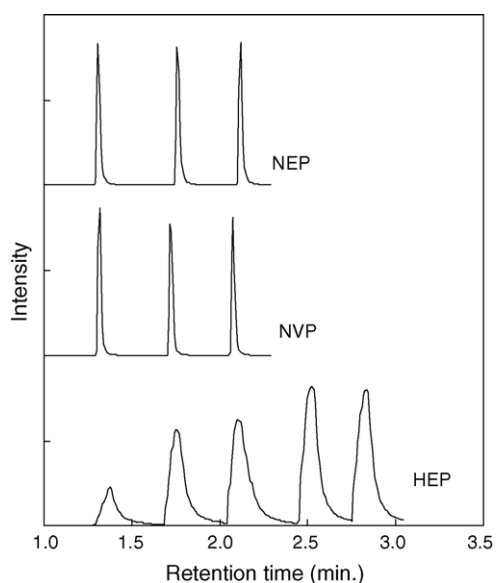


Fig. 4. Desorption peaks of each reagent in the pulse adsorption method. HEP peaks were magnified by five times.

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 $H_- = +9.4$.

3.5. Effect of reaction conditions

Fig. 3 shows the effects of GHSV and reaction temperature on the conversion of HEP under the following reaction

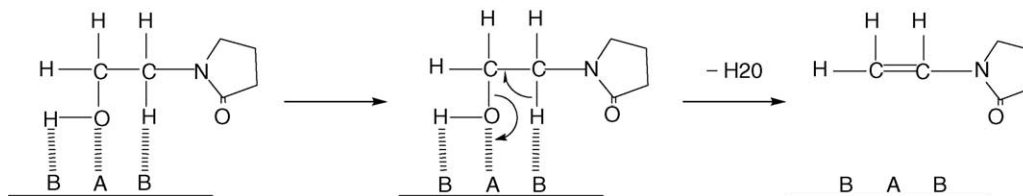


Fig. 5. Reaction mechanism proposed for the intramolecular dehydration of HEP to NVP. A, acid site (H^+ of silanol and/or alkali cation (M^+)); B, base site (O^{2-} bound to Si and/or alkali cation).

conditions: catalyst, Na₂O/SiO₂ (1/20); HEP concentration, 10 vol% in N₂.

At 360 °C, the conversion linearly increased with the contact time, indicating that the reaction rate followed 0 order with respect to HEP. As discussed later, the catalyst surfaces should be fully covered with HEP at this temperature, and the product NVP scarcely remained on the surfaces. At 370 and 380 °C, however, the relationships were not linear, indicating that the rates were positive orders with respect to HEP. From the initial rates at different temperatures, activation energy was calculated at 153.3 kJ/mol.

3.6. Features of catalysts

Adsorption and desorption behavior of HEP, NVP and *N*-ethyl-2-pyrrolidone (NEP) on the Na₂O/SiO₂ (1/20) catalyst at 300 °C was studied by a pulse method. NEP was used for the purpose of investigating the role of hydroxyl group in HEP, since a hydroxyl group in HEP is replaced by hydrogen in NEP.

As shown in Fig. 4, 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 peak of HEP showed a long tailing, which suggests that HEP is strongly adsorbed on the catalyst. On the other hand, the desorption peaks of NEP showed an intensity corresponding to the injection amount regardless of the pulse number, and had no long tailing. These results indicate that NEP is not strongly adsorbed on the catalyst. During the reaction of HEP, the surface active sites are fully covered with HEP, and NVP is desorbed immediately after it is formed by the intermolecular dehydration of HEP.

The adsorption behavior of NVP was similar to that of NEP, indicating that NVP was also adsorbed weakly on the catalyst. Considering the strong adsorption of HEP and weak adsorption of NEP, it is suggested that the strong adsorption of HEP is due to the interaction of OH group in HEP with the catalyst surfaces.

Adsorption of HEP and the successive reaction are proposed as shown in Fig. 5. HEP is first adsorbed on both base sites, O²⁻ in -OM and/or -OH, and acid sites (M⁺, H⁺) on the catalyst surface of M₂O/SiO₂ and then forms NVP by the intramolecular dehydration. Although the acidic strength of alkali metal oxide-added SiO₂ is very weak as measured by the indicator method, the role of the acid sites cannot be excluded. This reaction occurred on SiO₂ alone.

It is possible that the active sites are acid and base sites of hydroxyl group on SiO₂. This hydroxyl group can remain on alkali oxide/SiO₂ catalyst due to the amount of alkali oxide is not large enough to cover the SiO₂ surface. The acid sites presumably interact with the O atom of the OH group in HEP.

Table 2 shows the comparison of the catalytic performance of SiO₂ with that of alkali or alkaline earth metal oxide-added SiO₂. This suggests that an acidic catalyst shows a low activity while a basic catalyst shows much higher activity, the NVP selectivity being almost unchanged regardless of the activity. This tendency is not clear for the catalysts other than SiO₂. Probably, the acid site of silanol and/or silicate plays an important role in the catalytic performance.

4. Conclusions

- (1) We found that SiO₂ to which a small amount of alkali metal oxide was added exhibited a pronounced catalytic performance for the intramolecular dehydration of HEP to NVP in the vapor phase.
- (2) The HEP conversion decreased and the NVP selectivity increased with the increase in the ionization potential of the alkali element added to SiO₂.
- (3) For a good catalyst, the acid strength was weaker than $H_0 = +6.8$ and the base strength weaker than $H_- = +9.4$.
- (4) It is presumed that HEP is adsorbed on acid–base pair sites on the catalyst through the interaction of the hydroxyl group in the molecule with those sites, forming NVP by the intramolecular dehydration.

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