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Kinetic Studies on the Catalytic Synthesis of Benzyl Cyanide from 2-Phenylethanol and Ammonia

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Vapor-phase synthesis of benzyl cyanide from 2-phenylethanol and ammonia was studied over Ni-Cu-SiO₂ catalyst in the presence of hydrogen. Experiments were carried out in a flow reactor system under atmospheric pressure at 300°. The main product was benzyl cyanide, and toluene and phenethylamine were also produced. The Ni-Cu-SiO₂ catalyst (Ni/Cu=3/1) gave the best selectivity for benzyl cyanide, 80%. The deactivation of this catalyst was negligible.

By kinetic analysis, the rate of loss of 2-phenylethanol was found to show a first order dependency on the partial pressure of 2-phenylethanol, and was not affected by the partial pressures of ammonia and hydrogen. The experimental data were well interpreted by a model in which phenethylimine was produced as an intermediate and was then dehydrogenated to benzyl cyanide.

Keywords—vapor-phase synthesis; kinetics; reaction model; nickel-copper-silica gel catalyst; 2-phenylethanol; benzyl cyanide

Benzyl cyanide is important as a raw material for the synthesis of many kinds of drugs such as phenobarbital (a hypnotic sedative) and petidine (a synthetic analgesic).

The preferred synthetic method is a liquid-phase reaction in which a benzyl halide such as benzyl chloride is reacted with sodium cyanide. Various investigations on this reaction have been undertaken to raise the yield, and several patents exist.²⁾

However, there have been few reports on vapor-phase catalytic synthesis of benzyl cyanide. Ammoxidation is a well known synthetic reaction for aromatic nitriles, but the α -carbon of the side-chain is attacked under oxidative conditions, and benzonitrile is produced as a main product.³⁾ The reaction of aromatic alcohol with ammonia was studied over a Ni catalyst by Popov,⁴⁾ and nitriles were produced in 50% yield.

In the present study, we investigated the dehydrogenative condensation between 2-phenylethanol and ammonia over a Ni-Cu-SiO₂ catalyst in a stream of hydrogen. A model of the whole reaction, which has been examined by considering the yields of by-products, is presented.

Besides Popov's and this paper, a patent claiming that benzyl cyanide was obtained from 2-phenylethanol and ammonia in good yield is available,⁵⁾ but this patent is not concerned with the kinetics of the reaction.

Experimental

Materials—2-Phenylethanol, 3-cyanopyridine, ethylbenzene, methyl alcohol, Ni(NO₃)₂·6H₂O and Cu(NO₃)₂·3H₂O were purchased from Wako Pure Chemical Industries Ltd. and used as obtained. Benzene

1) Location: *Yoshida-Shimoadachi-cho, Sakyo-ku, Kyoto, 606, Japan.*

2) I. Kato, M. Takakura, and M. Hiraoka, (Nippon Soda Co., Ltd.) Japan. Kokai Patent 77111501 (1977) [(*C.A.*, **88**, 49762*f* (1978))]; F. Masuko, S. Hasegawa, and S. Nakai, (Sumitomo Chemical Co. Ltd.) Japan. Kokai Patent 7831642 (1978) [(*C.A.*, **89**, 108744*x* (1978))]; C. Harold, B.R. Lloyd, G. Roger, and K. Alan, (Albright and Wilson Ltd.) Brit. Patent 1336883 (1973) [(*C.A.*, **80**, 70564*n* (1974))].

3) Y. Kobayashi, Y. Kimura, M. Hosomi, K. Hattori, and K. Tarama, *Sekiyu Gakkai Shi*, **18**(3), 179 (1975); Y. Kobayashi, S. Shima, and K. Tarama, *ibid.*, **17**(4), 304 (1974).

4) M.A. Popov and N.I. Shuikin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1960**, 1451 [(*C.A.*, **55**, 448*c* (1961))].

5) K. Nakajima and T. Sato, (Nippon Synthetic Chemical Industry Co., Ltd.) Japan. Kokai Patent 7606939, 1976.

was obtained from Wako Pure Chemical Industries Ltd. and used after further purification. Ammonia and hydrogen were from commercial cylinders. Commercial silica gel from Nikki Kagaku Co., Ltd. was crushed and sieved (10–14 mesh) before use.

Catalyst—Silica gel which had been impregnated in a mixed solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was allowed to stand overnight: it was evaporated to dryness on a water bath and dried overnight at 110° . The total metal content was 0.1 atomic % (0.1 g-atom/100 g catalyst) in this work.

Procedure—The experiments were carried out in a tubular flow reactor system at atmospheric pressure and at 300° . The reaction rate was measured at low conversion and calculated by means of the following equation:

$$r_s = \frac{p_{s0}x's}{W/F}$$

where r_s ($\text{atm} \cdot \text{cm}^3 \cdot \text{g-cat}^{-1} \cdot \text{min}^{-1}$) is the disappearance rate of 2-phenylethanol, p_{s0} (atm) is the inlet partial pressure of 2-phenylethanol, $x's$ (–) is the conversion of 2-phenylethanol, W (g) is the weight of catalyst, and F ($\text{cm}^3 \cdot \text{min}^{-1}$) is the total flow rate. The partial pressure of 2-phenylethanol in the catalyst bed was assumed to be the average of the inlet and outlet partial pressures, and that of hydrogen or ammonia was assumed to be the inlet partial pressure throughout the reactor.

Mass transfer, both external and within the catalyst particles, was estimated to be sufficiently rapid that the reaction rate was not affected.

Analysis—For determination of the disappearance rate, analysis of inlet or outlet gas was carried out by injecting a 2 ml sample into a gas chromatograph (Yanagimoto Co. GCG-550T) connected to the reactor. In determining the yield of the main product or a by-product, the outlet gas from the integral reactor was absorbed in a vessel containing methanol and its composition was determined by gas chromatography using 3-cyanopyridine and ethylbenzene as internal standards. The column was packed with silicone DC 550 on Celite 545 BN (60/80 mesh) for every analysis. An appropriate column temperature was chosen for each analysis.

Results and Discussion

Catalyst

The synthesis of benzyl cyanide from 2-phenylethanol and ammonia was first tested over Ni-SiO₂ catalyst at 300° . Under these conditions, benzyl cyanide was produced in 50% yield, but the activity of this catalyst decreased rapidly within a few hours. Okada *et al.* reported that in the presence of hydrogen the dehydrogenative cyclization of diamine and alcohol produced N-heterocyclic compounds in good yields over a novel metal catalyst.⁶ Similarly, in the presence of hydrogen, the activity of the present catalyst increased and deactivation was almost negligible. The selectivity for benzyl cyanide, however, decreased to 30% in the presence of hydrogen due to decomposition of the main product to toluene.

It has now been shown that the addition of a group IB metal to a group VIII metal markedly decreases the activity of the latter for the rupture of carbon-carbon bonds in hydrogenolysis reactions of hydrocarbons, whereas it has a much smaller effect on other hydrocarbon reactions such as hydrogenation and dehydrogenation.⁷

In this work, an increase of benzyl cyanide selectivity was observed on adding Cu to Ni as shown in Fig. 1, where p_A and p_H are the partial pressures of ammonia and hydrogen, and the total amount of metal is 0.1 atomic % (0.1 g-atom/100 g catalyst). Evidently the maximum selectivity (80%) is obtained at Ni/Cu=3/1. Fig. 2 presents the activity of this optimal catalyst *versus* time-on-stream. The activity remained constant after the first 4 hours, and thus all the following experiments were carried out over this catalyst.

Kinetics

The rate of 2-phenylethanol loss was measured at various partial pressures of each reactant at low conversion. Figures 3 and 4 show, as logarithmic plots, the effects of the partial pressures. The rate of disappearance exhibited a first order dependency on the partial pressure

6) M. Tsuchiya, S. Morita, T. Tsukamoto, and J. Okada, *Yakugaku Zasshi*, **96**, 1005 (1976).

7) J.H. Sinfelt, *Progress in Solid-State Chemistry*, **10**, 55 (1975).

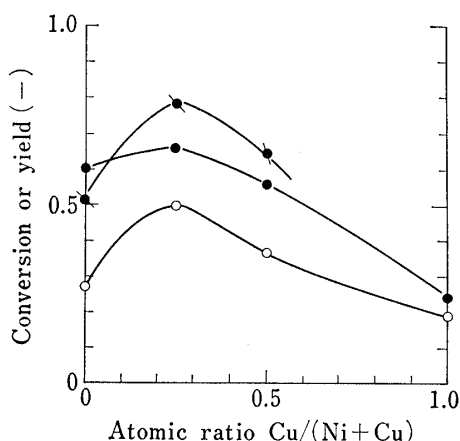


Fig. 1. Variations of Conversion, Yield and Selectivity as a Function of Composition of the Ni-Cu Catalyst

—●—: conversion, —○—: yield, —■—: selectivity.
Conditions: react. temp. = 300°, cat. (Ni-Cu-SiO₂) = 1.5 (g), p_{S_0} = 0.02 (atm), p_A = 0.20 (atm), p_H = 0.15 (atm), F = 50 (cm³·min⁻¹).

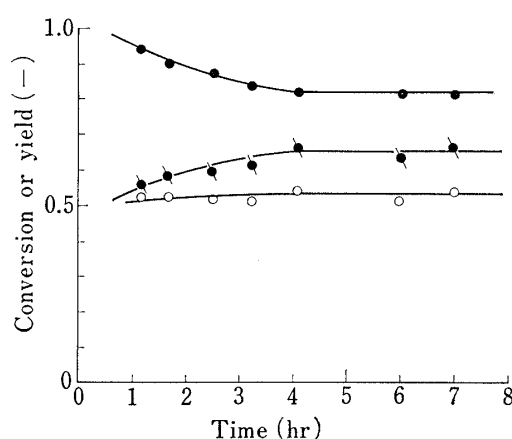


Fig. 2. Catalytic Activity *versus* Time-on-Stream

—●—: conversion, —○—: yield, —■—: selectivity.
Conditions: react. temp. = 300°, cat. (Ni-Cu-SiO₂) = 3.0 (g), p_{S_0} = 0.02 (atm), p_A = 0.20 (atm), p_H = 0.15 (atm), F = 50 (cm³·min⁻¹).

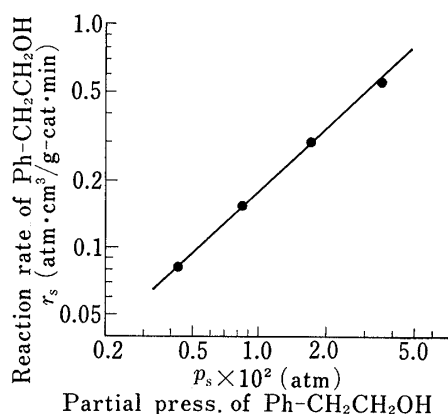


Fig. 3. Effect of Partial Pressure of 2-Phenylethanol

Conditions: react. temp. = 300°, cat. (Ni-Cu-SiO₂) = 2.0 (g), p_A = 0.40 (atm), p_H = 0.30 (atm), F = 100 (cm³·min⁻¹).

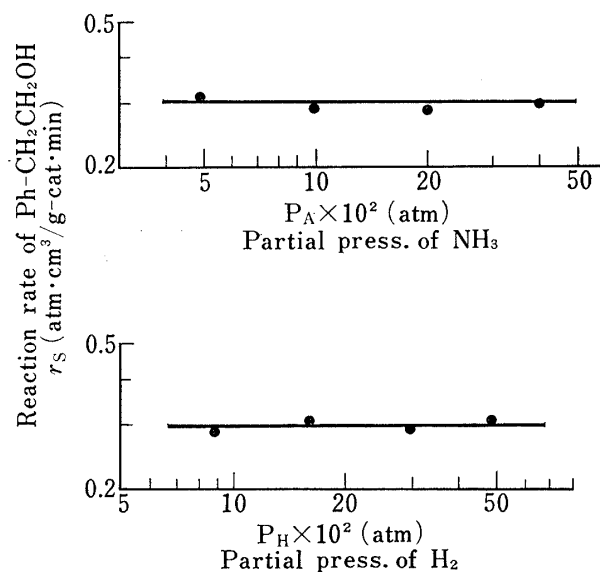


Fig. 4. Effects of Ammonia and Hydrogen

Conditions: react. temp. = 300°, cat. (Ni-Cu-SiO₂) = 2.0 (g), p_{S_0} = 0.02 (atm), F = 100 (cm³·min⁻¹); p_H = 0.30 (atm) or p_A = 0.4 (atm).

of 2-phenylethanol (Fig. 3). The rate was independent of the partial pressures of ammonia and hydrogen (Fig. 4).

In order to develop a reaction model, some experiments were carried out with various W/F values at constant partial pressures; the conversion and the yields of benzyl cyanide and toluene are plotted in Fig. 5. The results shown in Fig. 5. suggest that benzyl cyanide was decomposed to toluene and hydrogen cyanide⁸⁾ by hydrogenolysis. This was confirmed by another experiment in which benzyl cyanide was reacted as a starting material and toluene was produced. A trace of phenethylamine was detected as a by-product but was not analyzed quantitatively.

8) Hydrogen cyanide was detected as ammonium cyanide, but not analyzed quantitatively.

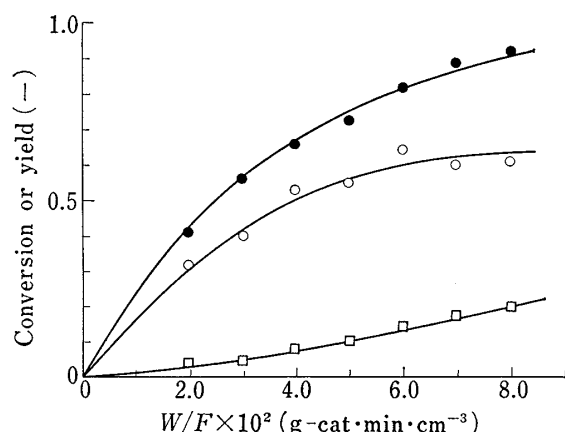


Fig. 5. Effect of Contact Time, W/F

—●—: conversion of $\text{Ph-CH}_2\text{CH}_2\text{OH}$, —○—: yield of $\text{Ph-CH}_2\text{CN}$, —□—: yield of Ph-CH_3 .
 Conditions: react. temp. = 300° , cat. (Ni-Cu-SiO_2) = 4.0 (g), p_{S_0} = 0.02 (atm), p_{A} = 0.40 (atm), p_{H} = 0.30 (atm).

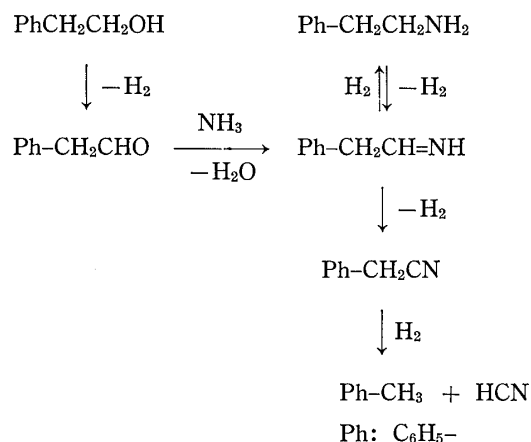
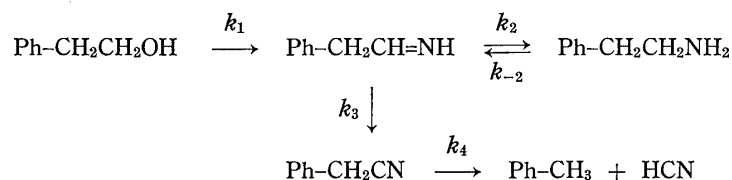


Chart 1. Reaction Model

The reaction model developed from these results is shown in Chart 1. Aldehyde, produced by dehydrogenation of 2-phenylethanol on the catalyst, reacts readily with ammonia and leads to phenethylimine. By-product phenethylamine is assumed to be formed reversibly by hydrogenation. Since the aldehyde was not detected, the reaction rate of aldehyde with ammonia is assumed to be very fast, and the model can be simplified as follows



The reaction rate of each component can be represented by the following equations (1) to (5), assuming that all the reactions are first order.⁹⁾ Equation (6) is a material balance equation.

$$dx_{\text{S}}/dt = -k_1x_{\text{S}} \quad (1)$$

$$dx_{\text{I}}/dt = k_1x_{\text{S}} - k_2x_{\text{I}} + k_{-2}x_{\text{A}} - k_3x_{\text{I}} \quad (2)$$

$$dx_{\text{A}}/dt = k_2x_{\text{I}} - k_{-2}x_{\text{A}} \quad (3)$$

$$dx_{\text{P}}/dt = k_3x_{\text{I}} - k_4x_{\text{P}} \quad (4)$$

$$dx_{\text{T}}/dt = k_4x_{\text{P}} \quad (5)$$

$$x_{\text{S}} + x_{\text{I}} + x_{\text{A}} + x_{\text{P}} + x_{\text{T}} = 1 \quad (6)$$

where x_{S} represents the unconverted fraction of $\text{Ph-CH}_2\text{CH}_2\text{OH}$, *i.e.*, $(1-x_{\text{S}})$ is the conversion of $\text{Ph-CH}_2\text{CH}_2\text{OH}$; x_{I} , x_{A} , x_{P} and x_{T} represent the yields of $\text{Ph-CH}_2\text{CH=NH}$, $\text{Ph-CH}_2\text{CH}_2\text{NH}_2$, $\text{Ph-CH}_2\text{CN}$ and Ph-CH_3 , respectively; t is the contact time, W/F ($\text{g-cat}\cdot\text{min}/\text{cm}^3$).

By using the stationary state method (with respect to phenethylimine), x_{A} and x_{I} can be eliminated and the following equations (7) to (9) obtained.

9) In this experiment, the partial pressures of hydrogen and ammonia were not changed and were regarded as constant because the gases were used in large excess. Therefore, the rate constants k_2 , k_{-2} , k_3 and k_4 , which may be functions of hydrogen and ammonia pressures, are assumed to be independent of them in the following analysis.

$$x_s = \exp(-k_1 t) \quad (7)$$

$$dx_p/dt = \beta \{k_1 x_s + k_{-2}(1 - x_s - x_p - x_T)\} - k_4 x_p \quad (8)$$

$$dx_1/dt = k_4 x_p \quad (9)$$

where

$$\beta = \frac{k_3}{k_2 + k_{-2} + k_3} \quad (10)$$

Comparing these equations with the experimental data, the values of k_1 , k_{-2} , β and k_4 can be calculated by the least-squares method. The results were as follows:

$$k_1 = 27.6 \text{ (cm}^3 \cdot \text{g-cat}^{-1} \cdot \text{min}^{-1}\text{)}$$

$$k_{-2} = 65.8 \text{ (cm}^3 \cdot \text{g-cat}^{-1} \cdot \text{min}^{-1}\text{)}$$

$$\beta = 0.644 \text{ (—)}$$

$$k_4 = 5.92 \text{ (cm}^3 \cdot \text{g-cat}^{-1} \cdot \text{min}^{-1}\text{)}$$

The calculated curves based on these values agree well with the experimental data (Fig. 5), and therefore it appears that the above model is adequate for this reaction.

Conclusion

These kinetic results provide valuable information about the vapor-phase synthesis of benzyl cyanide from 2-phenylethanol and ammonia.

In order to maintain the activity of Ni-SiO₂ catalyst, the reaction should be carried out in the presence of hydrogen. The hydrogenolysis of benzyl cyanide is depressed by adding Cu to the Ni catalyst, and the maximum selectivity is obtained at the ratio of 3:1 (Ni: Cu).

It is considered that this reaction is a dehydrogenative condensation of 2-phenylethanol with ammonia as shown in Chart 1, and our results are well interpreted by the rate equations (7) to (9).