Propionitrile formation from ethene and ammonia over Rh/Y-zeolite

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The Rh/Y-zeolite has been found to be more active and selective for propionitrile formation from ethene and ammonia than other transition metal supported Y-zeolites. A reaction between ethene and hydrogen cyanide has been proposed as a reaction route for propionitrile formation.

Keywords: Rh/Y-zeolite; propionitrile; ethene; ammonia; hydrogen cyanide

1. Introduction

More than 40 years ago, the reaction between an olefin (particularly propene) and ammonia (NH_3) was extensively studied [1–4]. In the case of ethene (C_2H_4) used as a reactant, acetonitrile (CH_3CN) was usually observed to be the main product. It was reported that Al_2O_3 was effective for CH_3CN formation from C_2H_4 and NH_3 [5]. Recently, we have reported that Zn^{2+} and Cd^{2+} exchanged Y-zeolites are more effective for this reaction than Al_2O_3 [6]. On the other hand, Yamauchi and Matsuda reported that propionitrile (C_2H_5CN) was formed from C_2H_4 and NH_3 besides CH_3CN over nickel or cobalt/kieselguhr catalysts [7]. Formation of C_2H_5CN from C_2H_4 and NH_3 is interesting, since both C–C bond scission in C_2H_4 and C–C bond formation are required in this reaction. The reaction route for C_2H_5CN formation, however, has not been clarified to date. In addition, other research on the formation of C_2H_5CN from C_2H_4 and NH_3 has not been reported. In the present work, we have found that Rh/Y-zeolite is very active for C_2H_5CN formation from C_2H_4 and NH_3, where C_2H_5CN is the dominant nitrile product.

2. Experimental

The Rh/Y-zeolite was prepared from rhodium trichloride trihydrate ($RhCl_3 \cdot 3H_2O$) in an aqueous solution and NaY-zeolite (Si/Al = 2.8) (obtained from Tosoh Corp.). After NaY-zeolite had been suspended in an aqueous solution of $RhCl_3$, the mixture was stirred at 323 K for 12 h. Other transition metal containing zeolites were prepared in a similar manner from the corresponding transition metal chlorides in an aqueous solution (Ni, Co) or in an ammonia aqueous solution (Cu, Pd). The powdery zeolites thus obtained were washed with distilled water, dried at 383 K overnight in an oven, and then stored in a closed container to expose them to water vapor over a saturated NH_4Cl aqueous solution at room temperature. The powder was pressed, crushed and then sieved to 20–42 mesh. A fixed-bed type reactor (a fused silica tube, i.d. = 10 mm) with continuous flow was operated at atmospheric pressure. The catalyst (1.000 g) was placed in the reactor and pretreated with hydrogen at 773 K for 3 h (the catalyst weight was 0.764 g after the pretreatment). The reaction was performed with the reaction gas mixture C_2H_4(20%)–NH_3(20%)–He(60%) (total flow rate = 50 $cm^3\ min^{-1}$). In order to identify the products, the reaction mixture was collected in a cold trap to be analysed by a GC-mass spectrometer. Reaction between butene (1-butene or mixture of trans- and cis-2-butene) and ammonia was performed in the same reactor system under similar reaction conditions. Reaction between ethene and hydrogen cyanide was carried out in a closed glass apparatus with a gas recirculating system (reaction volume = 320 cm^3). Concentrations of products in the reaction gas mixture were determined by gas chromatography.

3. Results and discussion

In the reaction between C_2H_4 and NH_3 over Rh/Y-zeolite, C_2H_5CN was predominantly formed. Formation of CH_3CN was also observed, but its amount was very small ($C_2H_5CN : CH_3CN = 94 : 6$). No appreciable formation of nitriles with higher molecular weights than C_3-nitrile was observed. Typical changes in rate of formation of C_2H_5CN (denoted by r_{PN}) are shown in fig. 1 on Rh/Y-zeolite (1.0 wt%), where r_{PN} decreased with time-on-stream. The rate of CH_3CN formation (denoted by r_{AN}) decreased with time-on-stream with almost the same decay pattern as r_{PN}. Selectivity to C_2H_5CN, estimated by ($2 \times C_2H_5CN$-formed)/($3 \times C_2H_4$-consumed), was about 80%. The color of the catalyst was gray after the pretreatment with H_2. After

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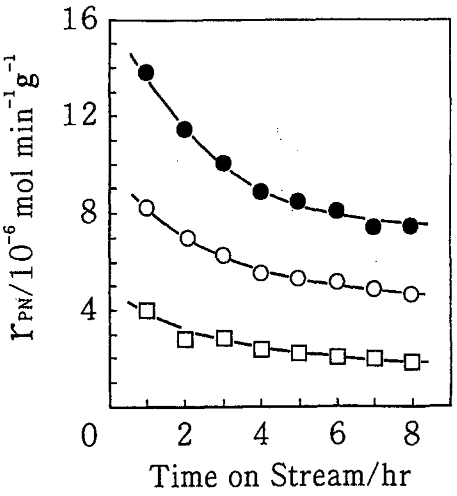

Fig. 1. Propionitrile formation from C_2H_4 and NH_3 over Rh/Y-zeolites (1.0 wt% Rh). (□) At 623 K; (○) at 673 K; (●) at 723 K.

the reaction the weight of the catalyst slightly increased (0.764 g → 0.804 g) and the color turned black, indicating coke formation on the catalyst during the reaction. The catalytic activity on the catalyst once used for the reaction was recovered in part by a pre-treatment of the catalyst with H_2 at 773 K for 3 h. However, a re-treatment of (O_2, 673 K, 3 h) → (H_2, 773 K, 3 h) further decreased the activity. In the present work, the catalytic activities were compared by using the rates of formation at time-on-stream of 5 h.

In table 1, the activities for C_2H_5CN and CH_3CN formation on other catalysts are compared with those on Rh/Y-zeolite. As shown by runs 1 and 2, Na/Y- and H/Y-zeolite were inactive for C_2H_5CN formation from C_2H_4 and NH_3, while some formation of CH_3CN was observed on the latter. As shown by runs 3 and 4, the activity for C_2H_5CN formation on Rh/Y-zeolite increased with an increase in the Rh loading, indicating that C_2H_5CN formation over Rh/Y-zeolite takes place at active rhodium sites. On Co/Y-, Ni/Y- and Cu/Y-zeolite, formation of both nitriles was observed, whereas the values for r_{PN} were much lower than that on Rh/Y-zeolite (in the case of Ni/Y-zeolite, a high activity for CH_3CN formation was observed). Although Pd/Y-zeolite was also found to be active for C_2H_5CN formation, r_{PN} on it was lower than r_{AN} ($C_2H_5CN : CH_3CN = 17 : 91$). The r_{PN} on Pd/Y-zeolite was much lower than that on Rh/Y-zeolite. For the catalysts examined, the Rh/Y-zeolite was found to be very effective for the selective formation of C_2H_5CN from C_2H_4 and NH_3.

Table 1
Reaction between C_2H_4 and NH_3 over various transition metal supported Y-zeolites

Run No.	Catalyst	Metal loading (wt%)	Activity[a] (10^{-6} mol min^{-1} g^{-1})	
			CH_3CN	C_2H_5CN
1	Na/Y	–	–[b]	–
2	H/Y	–	0.03	–
3	Rh/Y	1.0	0.38	5.28
4	Rh/Y	2.0	0.50	9.54
5	Co/Y	2.0	0.36	0.05
6	Ni/Y	2.0	2.47	0.31
7	Cu/Y	3.0	0.08	0.03
8	Pd/Y	2.0	0.91	0.17

[a] Rates of formation at time-on-stream of 5 h.
[b] Formation of nitrile was not observed.

Effects of reaction temperature on the catalytic activity of Rh/Y-zeolite can be seen from fig. 1. In the range of reaction temperature from 623 to 723 K, almost the same decay patterns in r_{PN} with time-on-stream were obtained, where r_{PN} increased with an increase in the reaction temperature. The apparent activation energy for C_2H_5CN formation was roughly estimated to be 50 kJ/mol. Effects of partial pressure of C_2H_4 or NH_3 on r_{PN} are shown in fig. 2. The r_{PN} decreased with an increase in C_2H_4 partial pressure as shown by open circles, whereas it increased with an increase in NH_3 partial pressure as shown by full circles. When the rate is expressed by a power-law form as $r_{PN} = kP^m_{C_2H_4}P^n_{NH_3}$, m and n are obtained as −0.2 and 0.6, respectively. The X-ray diffraction measurements of Rh/Y-zeolites prepared showed that the zeolite framework structure was not destroyed by supporting of rhodium chloride. However, a Rh/Al_2O_3 catalyst also showed a high catalytic activity for the C_2H_5CN formation with a high ratio for C_2H_5CN/CH_3CN (1.0 wt% Rh, $r_{PN} = 5.5 \times 10^{-6}$ mol min^{-1} g^{-1}, $C_2H_5CN : CH_3CN = 96 : 4$), indicating that the zeolite structure itself would not be required for the reaction to be catalysed.

The scission of a C–C bond is necessary for the formation of C_2H_5CN from C_2H_4 and NH_3, as well as the formation of a C–C bond. In case of reaction between propene (C_3H_6) and NH_3, CH_3CN has been observed to be the main product, where the following reaction route has been proposed [2–4]:

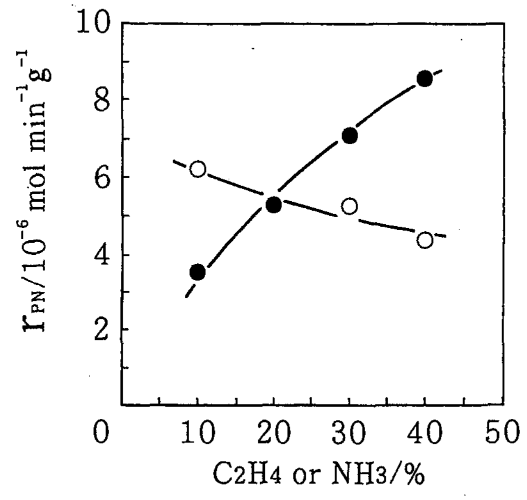

Fig. 2. Effects of partial pressure of C_2H_4 or NH_3 on the catalytic activity of C_2H_5CN formation over Rh/Y-zeolites (1.0 wt% Rh, at 673 K). (○) C_2H_4; (●) NH_3.

$$\begin{aligned} &CH_3CH{=}CH_2 + NH_3 \rightarrow [CH_3CH(NH_2)CH_3] \\ &\quad \rightarrow CH_3CN + CH_4 + H_2 \end{aligned}$$

The Rh/Y [8,9] and Pd/Y-zeolites [10] are known to be active catalysts for C_2H_4 dimerisation. Nickel has also been reported to be an active component for the dimerisation [11,12]. During the reaction between C_2H_4 and NH_3, in fact, butene (C_4H_8) was formed, while its amount was much less than that of the C_2H_5CN formed ($r_{C_4H_8} < 1 \times 10^{-9}$ mol min^{-1} g^{-1}). One of the possible reaction routes for the formation of C_2H_5CN from C_2H_4 and NH_3, therefore, may be a reaction between NH_3 and C_4H_8 which has been formed by ethene dimerisation. In this case, the reaction would be:

$$\begin{aligned} &2CH_2{=}CH_2 + NH_3 \rightarrow [CH_3CH_2CH(NH_2)CH_3] \\ &\quad \rightarrow CH_3CH_2CN + CH_4 + H_2 \end{aligned}$$

However, the amount of CH_4 formed in the reaction between C_2H_4 and NH_3 ($< 1 \times 10^{-7}$ mol min^{-1} g^{-1} at 673 K) was much less than that of C_2H_5CN formed (9.4×10^{-6} mol min^{-1} g^{-1} at 673 K).

The reaction between butene and NH_3 was carried out in the same flow apparatus under comparable reaction conditions with those in the reaction between C_2H_4 and NH_3. The following results were obtained: (1) r_{PN} ($r_{PN} \approx 3.4$ and 1.3×10^{-7} mol min^{-1} g^{-1} at 673 K for 1-butene and 2-butene, respectively) was much lower than that for the reaction between C_2H_4 and NH_3, (2) the nitrile product distribution was found to be very different from that in the reaction between C_2H_4 and NH_3 ($CH_3CN : C_2H_5CN = 2 : 3$ and $4 : 1$ for 1-butene and 2-butene, respectively), and (3) several by-products which were never observed in the reaction between C_2H_4 and NH_3 were formed in comparable amounts with C_2H_5CN. We also carried out C_2H_4 dimerisation over Rh/Y-zeolite. However, a catalytic activity of Rh/Y-zeolite for C_2H_4 dimerisation ($r_{C_4H_8} \approx 1 \times 10^{-9}$ mol min^{-1} g^{-1}) was much lower than that for C_2H_5CN formation (reaction conditions: He–C_2H_4(20%), 50 cm^3/min, at 673 K). In addition, the activity for C_2H_4 dimerisation decreased with an increase in the reaction temperature, as already reported [8,9]. These results indicate that C_2H_5CN was mainly formed through a reaction route other than the reaction between C_4H_8 and NH_3.

Another possible reaction route may be reaction between hydrogen cyanide (HCN) and C_2H_4, since a small amount of HCN was formed during the reaction. We have carried out the reaction between C_2H_4 and HCN in a closed system with a gas recirculating pump. The results obtained are shown in table 2, where the activities were evaluated by the amounts of nitriles formed during 2 h of reaction. As shown by runs 1 and 2, both Zn/Y- and Cd/Y-zeolites, which showed high activity for CH_3CN formation from C_2H_4 and NH_3, showed no appreciable activity for C_2H_5CN formation from C_2H_4 and HCN. Cu/Y-zeolite was found to be inactive for the C_2H_5CN formation as shown by run 3. Only a small amount of C_2H_5CN was formed on Ni/Y-zeolite as shown by run 4. However, Rh/Y-zeolite showed an excellent activity for C_2H_5CN formation as can be seen from runs 5 (at 513 K) and 6 (at 553 K), where no appreciable formation of CH_3CN was observed. These results strongly support that C_2H_5CN is formed by the reaction between C_2H_4 and HCN which has been formed by the reaction between C_2H_4 and NH_3. It is noteworthy that Pd/Y-zeolite, which was much less active for the formation of C_2H_5CN from C_2H_4 and NH_3 than Rh/Y-zeolite, also showed appreciable activity for C_2H_5CN formation from C_2H_4 and HCN, as shown by runs 7 (at 513 K) and 8 (at 553 K). These results indicate the important role of Rh/Y-zeolite in HCN formation from C_2H_4 and NH_3 in addition to the role of C_2H_5CN formation from C_2H_4 and HCN. In the case of CH_3CN formation from C_2H_4 and NH_3, ethylamine formation from C_2H_4 and NH_3 and subsequent decomposition of ethylamine into CH_3CN have been proposed as reaction route [2,3,5,6]. Even in the case of Ni/Y-zeolite which showed a high activity for CH_3CN formation (run 6 in table 1), C_2H_5CN was obtained as the main product in the reaction between C_2H_4 and HCN, indicating that the reaction mechanism for C_2H_5CN formation was different from that for CH_3CN formation.

Table 2
Reaction between C_2H_4 and HCN over various transition metal supported Y-zeolites [a]

Run No.	Catalyst	Reaction temperature (K)	Product [b] (10^{-3} mol)	
			CH_3CN	C_2H_5CN
1	Zn/Y	553	– [c]	–
2	Cd/Y	553	–	–
3	Cu/Y	553	–	–
4	Ni/Y	553	–	0.03
5	Rh/Y	513	–	0.06
6	Rh/Y	553	–	0.42
7	Pd/Y	513	–	0.02
8	Pd/Y	553	0.02	0.31

[a] Reaction conditions: catalyst = 0.100 g, $C_2H_4 = 1.7 \times 10^{-3}$ mol, and HCN = 1.7×10^{-3} mol.
[b] After 2 h of reaction.
[c] Formation of nitrile was not observed.

Rh/Y-zeolite has been found to be very effective for C_2H_5CN formation from C_2H_4 and NH_3 with a very high selectivity to C_2H_5CN. Although we have not clarified the reaction mechanism for HCN formation from C_2H_4 and NH_3 at the present time, the reaction between C_2H_4 and HCN is proposed to be a reaction route for the C_2H_5CN formation.

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