Mechanism of acrylonitrile decomposition over Cu-ZSM-5

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Abstract

The mechanism of acrylonitrile (AN) decomposition, that is, conversion of the nitrogen atoms in AN molecules to N_2, over Cu-ZSM-5 was investigated. Oxygen was found to be necessary for AN decomposition and H_2O in the reactant gas enhanced the reaction between AN and O_2. The dependence of AN decomposition on contact time indicated that HCN, HNCO, NH_3, and NO_x behaved like intermediates. Temperature-programmed surface reaction of adsorbed AN revealed that H_2O suppressed desorption of AN and lowered the temperature of N_2 evolution. In situ diffuse reflectance infrared Fourier transform spectroscopy revealed that AN was mostly converted to isocyanate (–NCO), which was probably converted to adsorbed NH_3 by hydrolysis. N_2 was formed by the reaction of adsorbed NH_3 and adsorbed nitrate or by oxidation of adsorbed NH_3.
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1. Introduction

Many kinds of volatile organic compounds (VOC) are becoming environmental problems because of their hazardous properties, such as carcinogenicity. For example, acrylonitrile (AN), a nitrogen-containing VOC, is reported to be carcinogenic [1]. Incineration and catalytic combustion are the most common methods for treatment of exhaust VOCs [2]. In the former case, the treatment temperature is too high to prevent NO_x ($NO + NO_2$) formation. The operation temperature for catalytic combustion is lower, but the effluent from nitrogen-containing compounds is liable to contain more-harmful nitrogen-containing byproducts, such as HCN [3]. Therefore, the development of a complete purification process for nitrogen-containing VOCs that produces only CO_2, H_2O, and N_2 is necessary.

We recently reported that Cu-ZSM-5 is a promising catalyst for the decomposition of AN [4,5]. This catalyst shows complete conversion of AN with a N_2 selectivity of 80% or more at temperatures higher than 350 °C. Isolated Cu^{2+} ions were determined to be the active sites and square planar type Cu^{2+} ions show particularly high activity. In addition, the redox property

between Cu^{2+} and Cu^+ is responsible for the catalytic activity. In this study, we focused on the mechanism of AN decomposition to form N_2 over Cu-ZSM-5.

2. Experimental

The details of the preparation method and the characteristics of the Cu-ZSM-5 used have been described elsewhere [5]. The catalyst used in this study was 2.3 wt% Cu-ZSM-5, which has an ion-exchange ratio of 57% and a specific surface area of $290 \, m^2/g$. It consists of isolated Cu^{2+} ions (square planar and square pyramidal) without a CuO phase and the extent of Cu^+ ions is small.

The catalytic activity was tested in a fixed-bed flow reactor system at atmospheric pressure. The catalyst (0.03–0.2 g) was placed in a tubular quartz reactor. The flow rate of the reactant gas was 100–280 ml/min, corresponding to W/F = 0.006–0.12 g s/ml (SV = 15,000–280,000 h^{-1}). The reactant gas was composed of approximately 200 ppm AN, 0–10% O_2, and 0–2% H_2O with He as a balance gas. Gaseous AN was supplied to the reactant gas by passage of a specified flow rate of He through liquid AN maintained at −18 °C. The effluent gas was analyzed by gas chromatography and Fourier transform infrared (FT-IR) spectroscopy. The gas chromatograph (Agilent; M200) was equipped with an MS-5A PROT column (for N_2 and CO analysis), a

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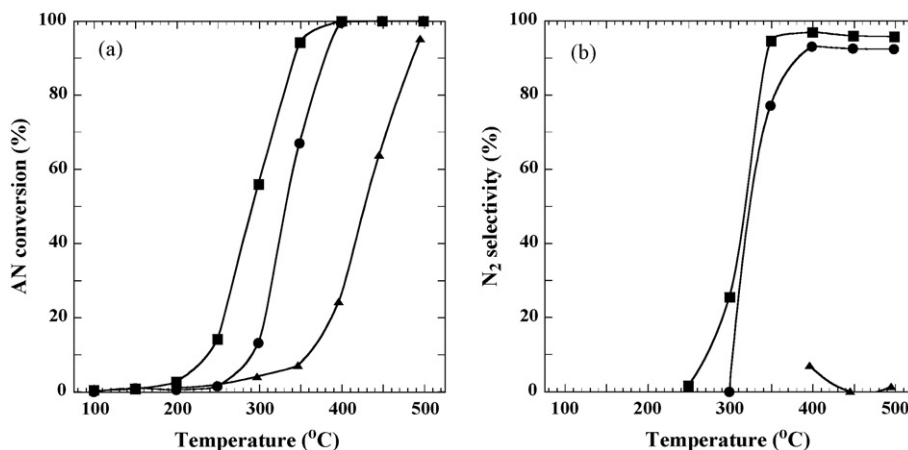 *E-mail address:* tty-namba@aist.go.jp (T. Nanba).

Fig. 1. Effect of feed gas composition on AN conversion (a) and N_2 selectivity (b) over Cu-ZSM-5: approximately 200 ppm AN + 5% O_2 (●), approximately 200 ppm AN + 5% O_2 + 0.5% H_2O (■), and approximately 200 ppm AN + 0.5% H_2O (▲). Catalyst weight, 0.1 g; flow rate, 160 ml/min.

PolaPROT Q column (for CO_2 and N_2O analysis), and a thermal conductivity detector for each column. An FT-IR spectrometer (Nicolet; Magna 560), which was equipped with a multireflection gas cell (Gemini Specialty Optics; Mercury Series, optical path length = 2 m), and a mercury cadmium telluride detector, was used for the analysis of gaseous NO, NO_2, AN, and other nitrogen-containing products.

Temperature-programmed surface reaction (TPSR) of adsorbed AN was carried out with the apparatus used for the activity tests. After pretreatment in 5% O_2 at 500 °C for 2 h, the sample was cooled to 50 °C in He, exposed to an AN flow (approximately 200 ppm) for 1 h, and then heated to 600 °C at 5 °C/min in 160 ml/min of 1% O_2 or 1% O_2 + 0.5% H_2O.

The changes in the surface species on the catalysts under conditions similar to those used for TPSR were observed by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with a Nexus 870 FT-IR spectrometer (Nicolet) equipped with a diffuse reflectance cell (Spectratech; Diffuse Reflectance 9067). The sample was pretreated in 5% O_2 at 500 °C for 30 min in the cell and then background spectra were obtained at 200 °C and room temperature in a 1% O_2/He flow.

Then AN was adsorbed at room temperature under an AN flow (approximately 300 ppm). After He purge for 15 min, the temperature was raised at 10 °C/min under a 1% O_2 or 1% O_2 + 0.5% H_2O flow. After a predetermined temperature above 200 °C was reached, the sample was cooled to 200 °C, and the spectrum was measured. Then the sample was heated again to a higher temperature than before and the spectrum was measured again.

3. Results and discussion

3.1. Effect of feed gas composition on AN decomposition activity

Fig. 1 shows the AN decomposition activity of Cu-ZSM-5 for three different feed gas compositions. The activity in the AN + O_2 + H_2O reaction was higher than that in the AN + O_2 reaction. The AN + H_2O reaction exhibited the lowest AN conversion and negligible N_2 formation. This result indicates that O_2 was essential for AN decomposition to N_2.

The effects of the concentrations of O_2 and H_2O in the AN + O_2 + H_2O reaction were investigated at 350 °C (Fig. 2).
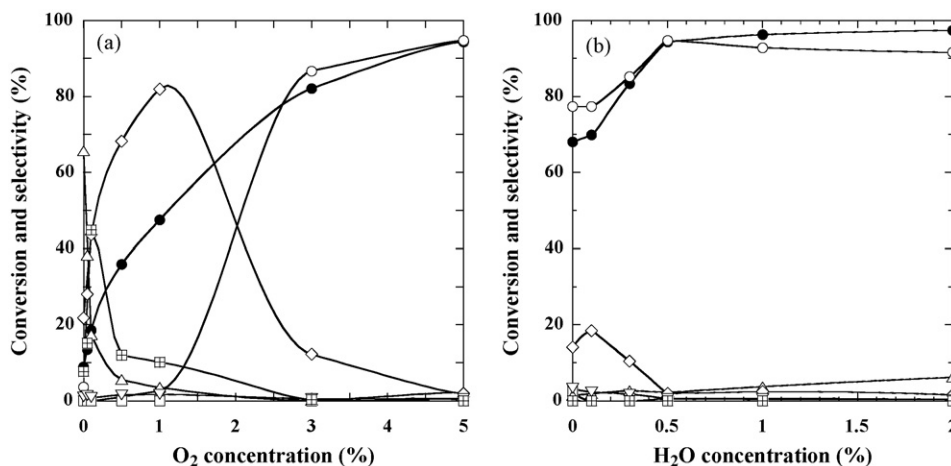

Fig. 2. Dependence of AN decomposition activity on the concentrations of O_2 (a) and H_2O (b): AN conversion (●) and selectivities of N_2 (○), N_2O (□), NH_3 (△), HCN (◇), HNCO (▽), and acetonitrile (⊞). Catalyst weight, 0.1 g; flow rate, 160 ml/min; feed gas approximately 200 ppm AN + 0–10% O_2 + 0–2% H_2O.

AN conversion increased with increasing O_2 concentration and N_2 formation became significant at O_2 concentrations higher than 2% (Fig. 2a). The major product in the absence of O_2 was NH_3, but the production of NH_3 decreased markedly as the O_2 concentration was increased. In contrast, HCN formation drastically increased with increasing O_2 concentration up to 1%. NH_3 formation in the absence of O_2 was evidently caused by AN hydrolysis. Since only 7.5 moles of O_2 is necessary for the complete oxidation of AN to form CO_2, H_2O, and N_2, an O_2 concentration of 3% should be sufficient for complete oxidation. No N_2 formation and significant acetonitrile and HCN formation below 3% suggest that O_2 reacted only with the C=C and C−C bonds at first. In other words, the vinyl group in AN had higher O_2 reactivity than the nitrile group.

Both AN conversion and N_2 selectivity increased with increasing H_2O concentration (Fig. 2b). HCN formation reached a maximum at 0.1% H_2O. NH_3 formation increased gradually but continuously with increasing H_2O concentration, which suggests that H_2O enhanced the hydrolysis reaction.

3.2. Dependence of AN decomposition activity on contact time

Fig. 3 shows the dependence of AN decomposition activity on contact time with the feed gas. In the absence of H_2O, AN conversion increased with increasing contact time up to 0.15 s (Fig. 3a). N_2 was not formed at contact times less than 0.056 s. The induction period for N_2 formation suggests that N_2 was formed via certain intermediates. The maximum HCN and HNCO concentrations were observed at 0.056 s. NO_x started to form after 0.056 s. N_2O production also had an induction period, longer than that of N_2. No NH_3 formation was observed. In the presence of H_2O, the trends for AN conversion and N_2, N_2O, HCN, and NO_x formation were similar to the trends in the absence of water, but there was a shift toward shorter contact times (Fig. 3b). In addition, NH_3 formation was observed with a peak at 0.075 s. Because the concentrations of HCN and HNCO

could be extrapolated to zero, we believe that these products were directly formed from AN. The induction period for the production of NH_3 indicates that it is not a direct product of AN. Because NO_x formation peaked at the same contact time as HCN and HNCO formation, NO_x might be formed directly from AN.

3.3. TPSR of adsorbed AN

We carried out TPSR of adsorbed AN to study its reactivity. Fig. 4 shows TPSR profiles for adsorbed AN with 1% O_2 or 1% O_2 + 0.5% H_2O. At 1% O_2, AN desorption began at around 100 °C and reached a maximum at 275 °C (Fig. 4a), at which temperature small amounts of CO_2 and CO were formed; substantial amounts of CO_2 and CO were formed at 410 and 390 °C, respectively. N_2 formation peaked at 420 °C. HCN and HNCO formation peaked at 350 and 380 °C, respectively, with the former having a secondary peak at 280 °C. N_2O formation occurred at almost the same temperature as N_2 formation. NO_x formation peaked at 250 and 350 °C. The total amount of AN adsorption was calculated from the total evolution of carbon, from which the rates of residual carbon and nitrogen on the surface at each temperature were estimated. Below 300 °C, the mole percentages of residual C and N were almost equal, but between 300 and 425 °C, residual C decreased earlier than residual N. The percentages of residual C and N became nearly equal after N_2 started to form. Below 300 °C, the lower-temperature peaks for HCN and NO_x evolution should be accompanied by oxidation of the vinyl group of adsorbed AN. Above 300 °C, the fact that residual C decreases earlier than residual N suggests that nitrogen atoms were retained in certain forms that were strongly bound to Cu-ZSM-5. These results indicate that N_2 was formed by reaction of adsorbed nitrogen-containing species.

When TPSR was carried out in 1% O_2 + 0.5% H_2O, the amount of AN desorbed decreased relative to the corresponding values for TPSR with 1% O_2, and the low-temperature peak for CO_2 evolution increased (Fig. 4b). CO_2, CO, and N_2 formation
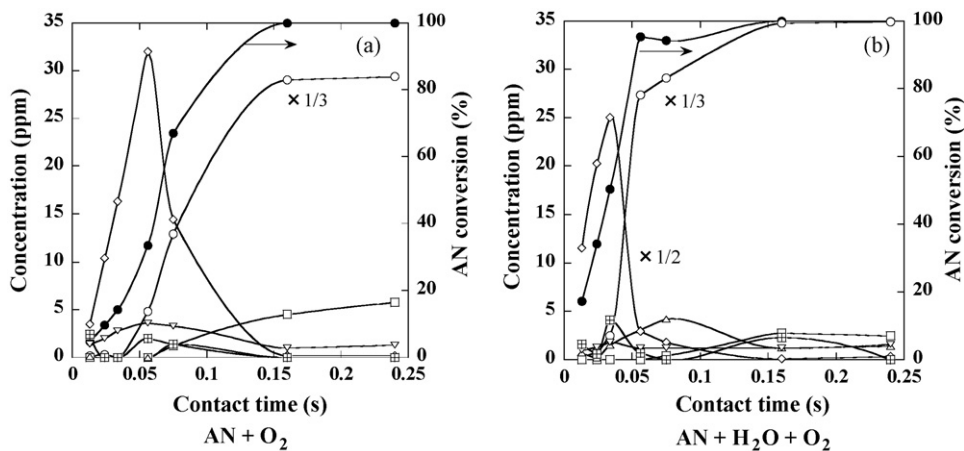

Fig. 3. Dependence of AN decomposition activity on contact time in the presence (a) and absence of H_2O (b): AN conversion (●) and concentrations of N_2 (○), N_2O (□), NH_3 (△), HCN (◊), HNCO (▽) and NO_x (⊞). Catalyst weight, 0.03–0.2 g; flow rate, 100–280 ml/min; feed gas, approximately 200 ppm AN + 5% O_2 + 0 or 0.5% H_2O.
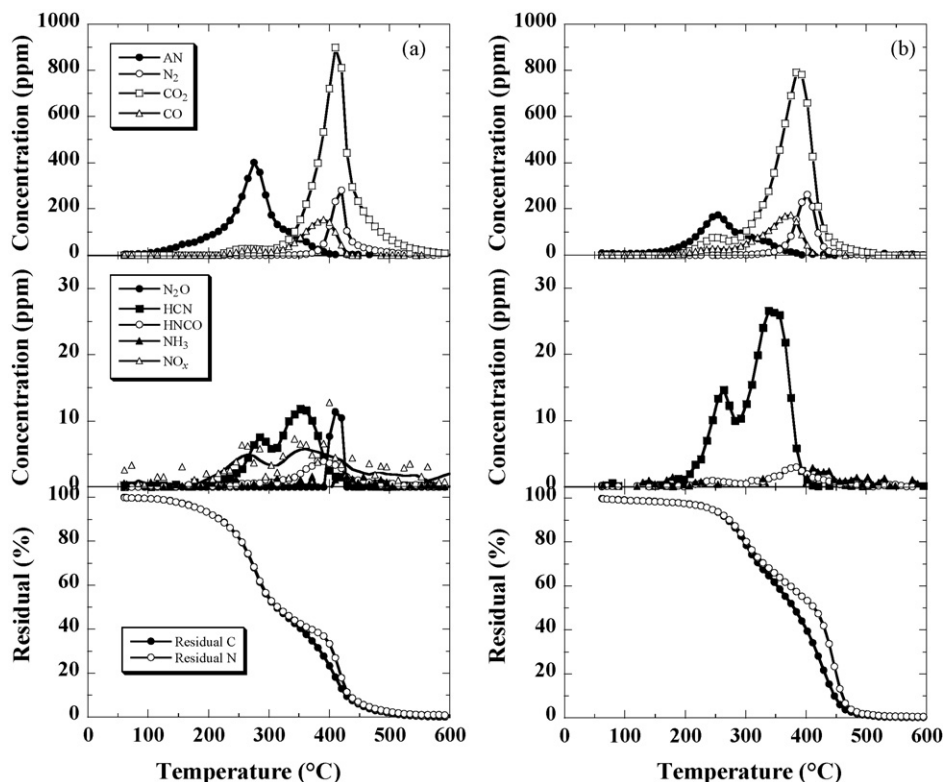
Fig. 4. Temperature-programmed surface reaction of adsorbed AN with 1% O_2 (a) and 1% O_2 + 0.5% H_2O (b). Catalyst weight, 0.1 g; flow rate, 160 ml/min; heating rate, 5 °C/min.

shifted about 20 °C toward lower temperatures. N_2O and NO_x were not formed, and HCN formation increased. NH_3 formation peaked at around 420 °C. In this case also, residual C became less than residual N above 300 °C and the difference between residual C and N was higher in the presence of H_2O than in the absence of H_2O. NH_3 evolution occurred at a higher temperature than N_2 formation, which suggests that NH_3 was strongly bound to Cu-ZSM-5.

3.4. DRIFTS measurements during TPSR

To identify surface intermediates, we carried out DRIFTS measurements under conditions similar to those used for TPSR in 1% O_2 (Fig. 5). At room temperature, absorption bands were observed at 3124–2991, 2306, 2283, 2258, and 1604 cm^{-1}. The absorbance of the 3124–2991 cm^{-1} bands decreased with increasing temperature. The absorbance of the 2306 cm^{-1} band initially increased slightly with increasing temperature, then started to decrease above 300 °C, and eventually disappeared above 400 °C. The band at 2258 cm^{-1} also disappeared at 250 and 300 °C, respectively. The band at 1604 cm^{-1} increased up to 300 °C and then decreased, but it did not disappear until 450 °C. The band at 2283 cm^{-1} shifted toward lower wavenumbers with increasing temperature and reached 2260 cm^{-1} at 400 °C. A new band appeared at 2157 cm^{-1} at 300 °C and this band increased with increasing temperature but decreased at 450 °C. A band at 3376 cm^{-1} appeared at 250 °C and disappeared above 450 °C. A band at 1625 cm^{-1} appeared at 200 °C and increased with increasing temperature but decreased at 450 °C.

The bands at 3124–2991 cm^{-1} have been ascribed to the vinyl group of AN [6]. The bands at 2283 and 2258 cm^{-1} have been ascribed to the stretching of the C≡N bond of AN [6,7]. The band at 1604 cm^{-1} observed at room temperature has been ascribed to the vinyl group of AN [7]. In our TPSR study, the band at 1604 cm^{-1} increased despite the fact that the vinyl group of AN decreased above 200 °C with increasing temperature. Therefore, the band at 1604 cm^{-1} above 200 °C should not be ascribed to the vinyl group. We believe that it should instead be ascribed
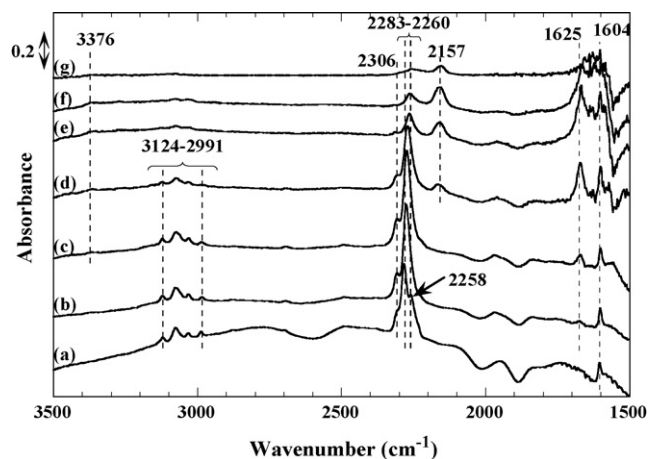

Fig. 5. In situ diffuse reflectance infrared Fourier transform spectra during TPSR with 1% O_2. AN adsorption was carried out at room temperature with approximately 300 ppm AN. (a) Room temperature, (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 350 °C, (f) 400 °C, and (g) 450 °C.

to molecularly adsorbed H_2O [8] and NH_3 adsorbed on Lewis acid sites [9–11]. NH_3 is known to be adsorbed on Cu^+ in ZSM-5, which is thought to be a Lewis acid site [12]. A weak band at 3376 cm^{-1} is regarded as additional evidence for adsorbed NH_3 [13,14]. The band at 2306 cm^{-1} has been also ascribed to AN adsorbed on Lewis acid sites [15], but in our study this band increased at first and then decreased with increasing temperature, which suggests that it overlaps with the band of other products, perhaps –NCO [16]. The disappearance of this band at 400 °C coincided with the peak for HNCO formation during TPSR measurement. The shift of the band at 2283 cm^{-1} toward lower wavenumber indicates the consumption of adsorbed AN and the formation of –NCO, since Solymosi et al. ascribed the band at 2260 cm^{-1} to Al^{3+}–NCO [16]. The band at 2157 cm^{-1}, which appeared above 300 °C, was due to Cu^+–CO [17–21]. The maximum absorbance was obtained at 400 °C and this result agrees with the maximum for CO formation in the TPSR results. The band at 1625 cm^{-1} was due to nitrate [6,22–25]. Nitrate was formed above 200 °C and disappeared at 450 °C. This behavior coincided with NO_x formation in TPSR with 1% O_2.

Fig. 6 shows the changes in the DRIFT spectra of preadsorbed AN as the temperature was increased in 1% O_2 + 0.5% H_2O. At room temperature, a new band appeared at 2240 cm^{-1} and then disappeared at 200 °C. The band has been variously assigned to the stretching vibration of C≡N in nitrile compounds [26], to N_2O [27,28], to –NCO [29], and to –CN [30]. Because no nitrogen-containing products evolved below 200 °C in our TPSR measurement, we believe that the band is probably due to C≡N stretching in nitrile compounds. The band at 2283 cm^{-1} shifted toward lower wavenumbers with increasing temperature, and at 200 °C the intensity of the band was markedly higher than that of the corresponding band in the spectrum in 1% O_2 (Fig. 5). This result suggests that AN conversion to isocyanate was enhanced by the presence of H_2O. In the presence of water, the band at 3376 cm^{-1} appeared above 200 °C, and the band was larger than that in the absence of H_2O (Fig. 5). This result suggests that H_2O enhanced the formation of adsorbed NH_3.
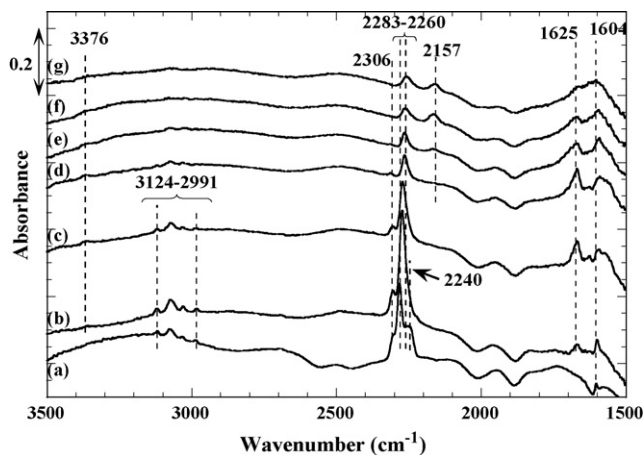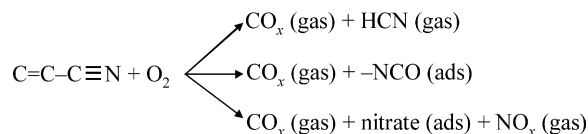

Fig. 6. In situ diffuse reflectance infrared Fourier transform spectra during TPSR with 1% O_2 + 0.5% H_2O. AN adsorption was carried out at room temperature with approximately 300 ppm AN. (a) Room temperature, (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 350 °C, (f) 400 °C, and (g) 450 °C.

3.5. Mechanism of AN decomposition

Our results clearly indicate that AN decomposition over Cu-ZSM-5 starts with oxidation of the vinyl group. The results shown in Fig. 2(a) seem to indicate that AN is directly hydrolyzed to form NH_3 in the absence of O_2. However, the large increase in AN conversion as well as acetonitrile and HCN formation upon the addition of O_2 (Fig. 2(a)) indicates that the reaction of O_2 with the vinyl group is much faster than the direct hydrolysis of the CN group. In other words, the predominant pathway for AN decomposition depends on whether O_2 is present or absent. In the presence of O_2, the residual species on the catalyst surface after the oxidation are expected to be –CN and –NCO, but DRIFTS measurements revealed that no –CN species were present. Below 300 °C, HCN was formed during TPSR, and –NCO and nitrate species increased in DRIFTS measurements, which suggests that initial AN decomposition may have proceeded via the following parallel reaction pathways:

$$C{=}C{-}C{\equiv}N + O_2 \begin{cases} CO_x \text{ (gas)} + \text{HCN (gas)} \\ CO_x \text{ (gas)} + \text{–NCO (ads)} \\ CO_x \text{ (gas)} + \text{nitrate (ads)} + NO_x \text{ (gas)} \end{cases}$$

We suspect that oxidation of the vinyl group was coupled with formation of –NCO and nitrate by means of oxidation of the nitrile group. H_2O addition enhanced AN conversion to gaseous HCN and surface isocyanate.

The results for the contact time dependence indicate that HCN behaves like an intermediate. In previous work, we confirmed that HCN is hydrolyzed over H-ferrierite and that HCN is converted to N_2 and NO_x in the presence of O_2 above 300 °C over Cu-ferrierite [31]. HCN hydrolysis may proceed on zeolite acid sites, but the reaction should soon be inhibited by NH_3, which is formed by hydrolysis and masks the acid sites [32]. Adsorbed CN species were not observed in DRIFTS measurements even under conditions in which significant HCN was formed, which suggests that the re-adsorption and subsequent reaction of HCN are negligible. The decrease in HCN formation at higher O_2 concentration (Fig. 2) and the fact that HCN behaves like an intermediate (Fig. 3) might be caused by the increase in the rate of other reaction pathways.

Isocyanate can be easily hydrolyzed to NH_3. We have reported that HNCO is hydrolyzed even below 100 °C [32]. Hydrolysis of –NCO is reported to form adsorbed NH_3 [14,33–35], and oxidative conversion of –NCO to N_2 proceeds over Cu-ZSM-5 [36]. In the present DRIFTS measurements, the absorbance for adsorbed NH_3 in the presence of H_2O increased with increasing temperature, and at the same time –NCO decreased with increasing temperature. The maximum absorbance of adsorbed NH_3 was observed at 300–400 °C, at which temperature the preferential decrease of residual C relative to residual N became significant. Therefore, the subsequent reaction of –NCO seems to release C but retain N on Cu-ZSM-5.

Nitrate is known to react with NH_3 to form N_2 over Cu-ZSM-5 in the presence of O_2 [37]. Our results for the dependence of the catalytic performance on contact time showed that NO_x formation showed a maximum, indicating that nitrate must be

a precursor of NO_x formation and also an intermediate of N_2 formation. NO_x reduction by NH_3 over Cu-ZSM-5 is known to exhibit high N_2 selectivity with small amounts of N_2O formation [13,38,39]. Indeed, in our TPSR experiments in 1% O_2 + 0.5% H_2O, NO_x and N_2O were not formed. The subsequent reaction of nitrate may have been involved in the formation of N_2O.

NH_3 not only reacts with nitrate but also undergoes oxidation to produce N_2. The reaction of nitrate and NH_3 to form N_2 requires comparable amounts of both species, and the increase in adsorbed NH_3 in the presence of H_2O leads to there being an insufficient amount of nitrate to produce N_2. We have reported that Cu-ZSM-5 has high NH_3 oxidation activity with high N_2 selectivity [4] and that some portion of the NH_3 is more strongly adsorbed on Cu-ZSM-5 than on H-ZSM-5 [5]. We suspect that the increase in residual N during TPSR in the presence of H_2O resulted from the increase in adsorbed NH_3, which was formed mainly by –NCO hydrolysis and may have been selectively converted to N_2.

In light of the considerations mentioned above, we propose the mechanism for AN decomposition over Cu-ZSM-5 presented in Fig. 7. AN decomposition is initialized by oxidation of the vinyl group to form gaseous HCN and NO_x and surface –NCO and nitrate species. The isocyanate species is hydrolyzed to NH_3. N_2 is formed by the reaction between adsorbed NH_3 and nitrate and by oxidation of adsorbed NH_3. Poignant et al. have suggested that AN decomposition over Cu-ZSM-5 proceeds via AN adsorption $\rightarrow$ Cu^+–CN $\rightarrow$ Cu^+–NC $\rightarrow$ Cu^+–NCO $\rightarrow$ Cu^+–NH_3 and that the adsorbed NH_3 then reacts with NO to form N_2 [6]. NH_3 formation and subsequent reaction to form N_2 should be necessary steps for N_2 formation. We speculate that the active sites of Cu-ZSM-5 for AN decomposition are isolated Cu^{2+} ions and that the redox reaction between Cu^{2+} and Cu^+ is indispensable [5]. Llabrés et al. have suggested that reoxidation of Cu^+ is promoted by H_2O addition [40]. The enhancement of AN reactivity by the addition of H_2O is probably due to the promotion of re-oxidation of Cu^+. Square planar Cu^{2+} ion is known to have high oxidation activity [41]. We suspect that Cu^{2+} ion sites are necessary for oxidation of AN.
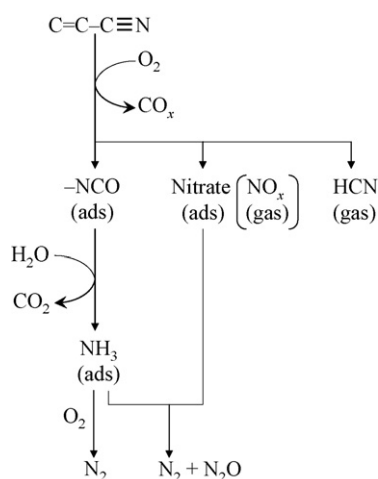

Fig. 7. Proposed mechanism of AN decomposition to form N_2.

4. Conclusion

We investigated the mechanism of acrylonitrile (AN) decomposition, particularly the conversion of the nitrogen atom in AN to N_2, over Cu-ZSM-5. The dependence of AN decomposition on the feed gas composition indicated that O_2 was necessary for N_2 formation and that H_2O enhanced the reaction of AN and O_2. The dependence of AN decomposition on oxygen concentration indicated that excess O_2 relative to AN was necessary for N_2 formation. The formation of acetonitrile and HCN at low O_2 concentrations suggested that AN decomposition was initiated by oxidation of the vinyl group of AN. The dependence of AN decomposition on contact time led us to suspect that N_2 formed via certain intermediates, because N_2 formation exhibited an induction period. HCN, HNCO, NH_3, and NO_x behaved like intermediates. In the presence of H_2O, the formation of all the products shifted toward shorter contact times. TPSR of adsorbed AN in 1% O_2 showed that N_2 formation became significant above 300 °C and that small amounts of CO_2, HCN, HNCO, and NO_x were formed along with AN desorption below 300 °C. Estimation of the ratio of the amounts of residual C and residual N during TPSR revealed that these amounts were almost equal below 300 °C but that more N than C remained at temperatures above 300 °C. The addition of H_2O to the reactant gas decreased the desorption of AN in TPSR and increased the amount of residual N above 300 °C. DRIFTS measurements under conditions similar to those used for TPSR revealed that the adsorbed AN was converted to isocyanate. The isocyanate species may have been hydrolyzed to adsorbed NH_3. The presence of H_2O enhanced the formation of isocyanate and adsorbed NH_3. On the basis of these results, we suspect that the mechanism of AN decomposition to N_2 over Cu-ZSM-5 proceeds via oxidation of the vinyl group of AN to form isocyanate, which is hydrolyzed to adsorbed NH_3. N_2 may be formed by oxidation of NH_3 and by reaction between adsorbed NH_3 and adsorbed nitrate.

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