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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.

Keywords: Acrylonitrile; Decomposition; Cu-ZSM-5; Isocyanate; Oxidation; Hydrolysis

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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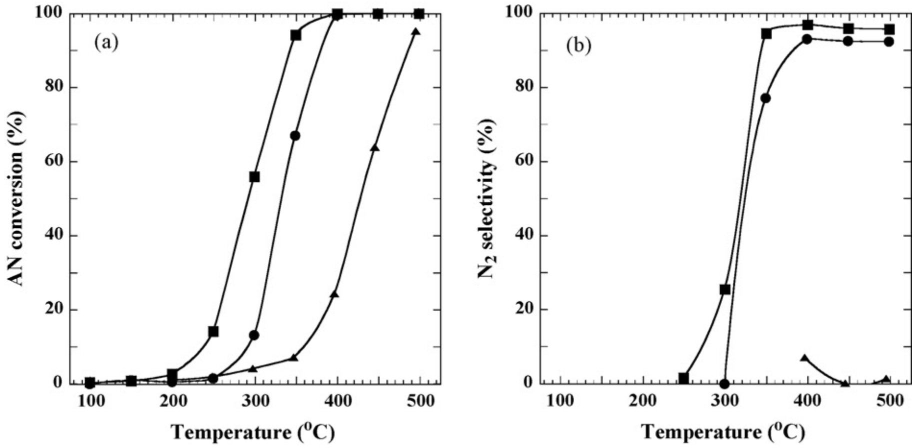

Fig. 1. Effect of feed gas composition on AN conversion (a) and N_2 selectivity (b) over Cu-ZSM-5: approximately 200 ppm AN + 5% O_2 (●), approximately 200 ppm AN + 5% O_2 + 0.5% H_2O (■), and approximately 200 ppm AN + 0.5% H_2O (▲). Catalyst weight, 0.1 g; flow rate, 160 ml/min.

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).

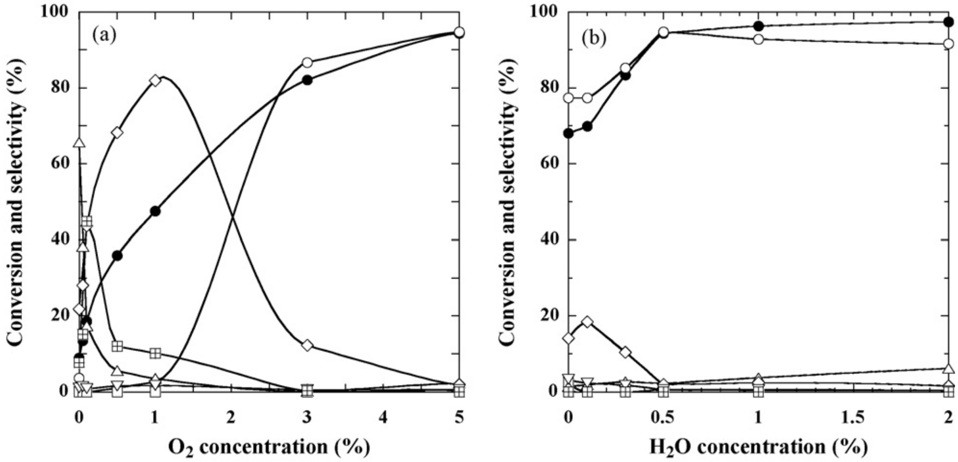

Fig. 2. Dependence of AN decomposition activity on the concentrations of O_2 (a) and H_2O (b): AN conversion (●) and selectivities of N_2 (○), N_2O (□), NH_3 (△), HCN (◇), HNCO (▽), and acetonitrile (⊞). Catalyst weight, 0.1 g; flow rate, 160 ml/min; feed gas approximately 200 ppm AN + 0–10% O_2 + 0–2%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