

# Active sites of Cu-ZSM-5 for the decomposition of acrylonitrile

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## Abstract

The catalytic decomposition of acrylonitrile (AN) over Cu-ZSM-5 prepared with various Cu loadings was investigated. AN conversion, during which the nitrogen atoms in AN were mainly converted to N<sub>2</sub>, increased as Cu loading increased. N<sub>2</sub> selectivities as high as 90–95% were attained. X-ray diffraction measurements (XRD) and temperature-programmed reduction by H<sub>2</sub> (H<sub>2</sub>-TPR) showed the existence of bulk CuO in Cu-ZSM-5 with a Cu loading of 6.4 wt% and the existence of highly dispersed CuO in Cu-ZSM-5 with a Cu loading of 3.3 wt%. Electron spin resonance measurements revealed that Cu-ZSM-5 contains three forms of isolated Cu<sup>2+</sup> ions (square-planar, square-pyramidal, and distorted square-pyramidal). The H<sub>2</sub>-TPR results suggested that in Cu-ZSM-5 with a Cu loading of 2.9 wt% and below, Cu<sup>+</sup> existed even after oxidizing pretreatment. The activity of AN decomposition over Cu/SiO<sub>2</sub> suggested that CuO could form N<sub>2</sub>, but, independent of the CuO dispersion, nitrogen oxides (NO<sub>x</sub>) were formed above 350 °C. Cu<sup>+</sup> and the square-pyramidal and distorted square-pyramidal forms of Cu<sup>2+</sup> showed low activity for AN decomposition. Temperature-programmed desorption of NH<sub>3</sub> suggested that N<sub>2</sub> formation from NH<sub>3</sub> proceeded on Cu<sup>2+</sup>, resulting in the formation of Cu<sup>+</sup>. The Cu<sup>+</sup> ions were oxidized to Cu<sup>2+</sup> at around 300 °C. Thus, high N<sub>2</sub> selectivity over Cu-ZSM-5 with a wide range of temperature was probably attained by the reaction over the square-planar Cu<sup>2+</sup>, which can be reversibly reduced and oxidized.

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## 1. Introduction

Acrylonitrile (AN) is an important raw material for the production of various chemicals and polymers. It is used to make acrylic fibers, resins (acrylonitrile–butadiene–styrene and styrene–acrylonitrile resins), and nitrile elastomers and is employed as an intermediate in the production of adiponitrile and acrylamide [1]. However, AN, which is classified as a volatile organic compound (VOC), is a hazardous and carcinogenic chemical [2]; in Japan, its permitted threshold limit in working environments is as low as 2 ppm. It is strongly demanded to prevent its emission into the atmosphere.

Thermal combustion and catalytic combustion are useful methods for treating exhaust gases containing AN and other VOCs [3]. However, in the former method, the operating

temperature is too high to prevent formation of thermal nitrogen oxides (NO<sub>x</sub>) (NO + NO<sub>2</sub>), and in the latter method, although the operating temperature is relatively low, the effluent gas might contain NO<sub>x</sub> (produced by excess oxidation of the nitrogen atoms in AN) and more-harmful products, such as HCN, derived from the nitrile group in AN [4]. To avoid these problems, it is necessary to develop a catalytic process that safely enables complete decomposition of AN, that is, a process producing only CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> as final products. In this ideal process, nitrogen atoms in the AN molecules are oxidized to N<sub>2</sub>, but not NO<sub>x</sub>, while the carbon atoms are oxidized completely to CO<sub>2</sub>. Catalysts having a too strong oxidation ability are undesirable.

Only a few reports have addressed the importance of the complete decomposition of AN. Gervasini et al. reported that Ba–Cu–Cr/Al<sub>2</sub>O<sub>3</sub> catalyst combined with the use of ozone can abate AN effectively [5]. Li et al. reported that non-noble-metal catalysts (mixtures of La, Ce, Ni, Co, and Mn) supported on Al<sub>2</sub>O<sub>3</sub> have a higher activity for AN

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decomposition than noble-metal catalysts (mixtures of Pt and Pd) [6]. However, these reports focused on the conversion of AN, not N<sub>2</sub> selectivity.

We recently reported that Cu-ZSM-5 is a promising catalyst for the decomposition of AN [7]. This catalyst completely converted AN with an N<sub>2</sub> selectivity of 80% or more at 350 °C and above. We speculated that Cu<sup>+</sup> in Cu-ZSM-5 was involved in the formation of N<sub>2</sub>. Cu-ZSM-5 has been extensively studied as a promising catalyst for the abatement of NO<sub>x</sub> in combustion exhaust gases [8–14]. In the selective catalytic reduction of NO<sub>x</sub> by hydrocarbons, AN has been regarded as a possible intermediate to form N<sub>2</sub>. Poignant et al. proposed a mechanism for the decomposition of AN over Cu<sup>+</sup> in partially protonated Cu-ZSM-5 to ethylene and cyanides during the selective catalytic reduction of NO<sub>x</sub> by propane [15]. Gerlach et al. reported hydrolysis of AN to NH<sub>3</sub> over acidic zeolites [16]. Hayes et al. reported that adsorbed nitriles on Cu-ZSM-5, which were derived from acetonitrile, can be converted to CO<sub>2</sub> and N<sub>2</sub> in the presence of oxygen [17].

In this study, we focused on the decomposition of AN over Cu-ZSM-5 catalysts of various Cu loadings to form N<sub>2</sub> without the formation of NO<sub>x</sub>. Changing the Cu loadings and preparation procedures created different combinations of Cu species in the Cu-ZSM-5 catalysts. To determine the Cu species that were most active in N<sub>2</sub> formation, we physically characterized the various species and evaluated their catalytic activities.

## 2. Experimental

### 2.1. Preparation of catalysts

Five grams of NH<sub>4</sub>-ZSM-5, prepared from Na-ZSM-5 (HSZ-820-NAA, Tosoh) by ion exchange in aqueous NH<sub>4</sub>NO<sub>3</sub>, was immersed in 100 mL of an aqueous solution of Cu(CH<sub>3</sub>COO)<sub>2</sub> (Wako) at 80 °C for 24 h with stirring. The slurry was then filtered, washed with distilled water, and dried at 110 °C overnight; the Cu-loaded zeolite was then calcined in air at 500 °C for 4 h. Various Cu loadings were obtained by using various concentrations of Cu(CH<sub>3</sub>COO)<sub>2</sub>. In addition, ion exchange with Cu(CH<sub>3</sub>COO)<sub>2</sub> was carried out at room temperature according to the procedure of Iwamoto et al., with pH adjusted to ca. 7 [18,19]. The Cu-ZSM-5 thus formed is expressed as Cu-ZSM-5(rt).

Cu/SiO<sub>2</sub> was prepared by both the impregnation and sol-gel methods. With the impregnation method, Cu(NO<sub>3</sub>)<sub>2</sub> (Wako) and SiO<sub>2</sub> (Wakogel C-100, Wako; 438 m<sup>2</sup>/g) were used as precursors. The Cu loading as metal was adjusted to 5 wt%. The catalyst was finally calcined at 500 °C in air for 4 h. With the sol-gel method, tetraethyl orthosilicate (TEOS) and H<sub>2</sub>O were mixed in a molar ratio of 1:4. Ethylene glycol was added to the Cu(NO<sub>3</sub>)<sub>2</sub> aqueous solution in a molar amount equivalent to that of Cu. These solutions were mixed and refluxed at 80 °C until gelation

was achieved. The gel was dried at 110 °C for 12 h under an air flow, and then calcined at 500 °C for 4 h under an air flow. The Cu loading as metal was adjusted to 5 wt%. Cu/SiO<sub>2</sub> prepared by the impregnation method is expressed as Cu/SiO<sub>2</sub>(I) and Cu/SiO<sub>2</sub> prepared by the sol-gel method is expressed as Cu/SiO<sub>2</sub>(SG).

### 2.2. Activity test

Catalytic activity tests were carried out with a fixed-bed flow reactor system at atmospheric pressure. The weight of catalyst placed in the quartz tube (inner diameter = 8 mm) of the reactor was 0.1 g. The flow rate of the reactant gas was 160 mL/min, which corresponds to  $W/F = 0.0375$  g s/mL. The reactant gas consisted of ca. 200 ppm AN, 5% O<sub>2</sub>, and 0 or 0.5% H<sub>2</sub>O with He as a balance gas. AN was introduced into the reactant gas stream by passing a predetermined flow rate of He through AN liquid maintained at –18 °C.

The effluent gas was analyzed by gas chromatography and FT-IR spectrometry. The gas chromatograph (Agilent; MicroGC) was equipped with an MS-5A PROT column for N<sub>2</sub> and CO analysis, a PolaPROT Q column for CO<sub>2</sub> and N<sub>2</sub>O analysis, and thermal conductivity detectors for each column. An FT-IR spectrometer (Nicolet; Magna 560), equipped with a multireflection gas cell (Gemini Specialty Optics; Mercury Series, optical path length = 2 m) and an MCT detector, was used for the analysis of AN and nitrogen-containing products. The FT-IR measurements were performed with a resolution of 0.5 cm<sup>-1</sup>, and each spectrum was obtained by accumulating 50 scans.

AN decomposition was also investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), using a Nexus 870 FT-IR spectrometer (Nicolet) equipped with a diffuse reflectance cell (Spectratech; Diffuse Reflectance 9067). The sample was pretreated in 5% O<sub>2</sub> at 500 °C for 2 h. The feed gas composition was the same as that used for the catalytic activity test; the reaction temperature was set at 350 °C. The background spectra were obtained with a He flow at 350 °C. The measurements were performed with a resolution of 4 cm<sup>-1</sup>, and a spectrum was obtained by accumulating 128 scans.

### 2.3. Characterization

The BET specific surface areas of the catalysts were measured by N<sub>2</sub> adsorption at –196 °C (Nikkisou, Model 4232) under a flow condition at atmospheric pressure. The Cu loadings of the zeolitic catalysts were determined by using inductively coupled plasma emission spectroscopy (Seiko Electronics, SPS 1200A). The procedure for temperature-programmed reduction by H<sub>2</sub> (H<sub>2</sub>-TPR) has been described elsewhere [7]. Electron spin resonance (ESR) analysis was carried out with a JEOL TE300 instrument. All samples were heated at 200 °C for 2 h in vacuo before ESR measurement, which was carried out in vacuo at room temperature. Spin concentrations were

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