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Effect of support materials on Ag catalysts used for acrylonitrile decomposition

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ABSTRACT

The effect of the support material on the Ag-catalyzed decomposition of acrylonitrile (AN) to form N_2 was studied for catalyst systems of Ag-ZSM-5, Ag/Al_2O_3, Ag/TiO_2, Ag/SiO_2, Ag/MgO, and Ag/ZrO_2. Ag/TiO_2 and Ag/SiO_2 exhibited high AN conversion with high N_2 selectivity. X-ray diffraction, ultraviolet–visible spectroscopy, and H_2 temperature-programmed reduction revealed that both metallic and oxidized Ag species were present on TiO_2 and SiO_2. On the basis of diffuse reflectance infrared Fourier transform spectroscopy measurements, NH_3 appeared to be formed by hydrolysis of AN, and this hydrolysis was enhanced by the presence of oxidized Ag species in the catalysts. The high AN decomposition activity was due to the presence of both oxidized and metallic Ag species, which promoted the hydrolysis of AN to form NH_3 and the subsequent oxidation of NH_3 to N_2, respectively.

1. Introduction

Emission control of volatile organic compounds (VOCs) is important, because many VOCs have hazardous properties [1]. Incineration is a simple way to remove VOCs, but the process is normally operated at high temperatures, around 800 °C [2]. Catalytic oxidation can decrease the operation temperature for incineration, and such catalytic removal has been studied extensively [3]. Recently, combinations of catalysts with ozone and plasma also have been studied as a means to further decrease incineration temperatures [4,5].

VOCs include many nitrogen-containing compounds. The presence of these nitrogen atoms causes the formation of harmful byproducts during incineration; for example, incineration and catalytic oxidation cause the formation of nitrogen oxides (NO_x) [2,6]. Some catalytic treatments generate other nitrogen-containing compounds, such as HCN [7]; therefore, the conversion of nitrogen in VOCs to inert products, such as N_2, is highly desirable.

In this report, we focus on the catalytic removal of acrylonitrile ($CH_2{=}CH{-}C{\equiv}N$; referred to herein as AN), because AN is known to be a carcinogenic VOC [8]. AN is a raw material of resins, such as acrylonitrile–butadiene–styrene and acrylonitrile–styrene, and a raw material for the synthesis of chemicals, such as acrylic acid or acrylamide. AN has a vapor pressure of 23.1 Torr at 0 °C, and its half-life in the atmosphere is estimated to be 2–3 days. These values are greater than those of benzene, which is also known to be carcinogenic [9]. The threshold limit of AN in work environments is as low as 2 ppm in the United States and Japan. Furthermore, AN is specified in Japan as one of 22 kinds of harmful pollutants for which primary efforts to prevent release into the atmosphere should be made. Therefore, the development of both a treatment system for local exhaust gas containing AN and a method for controlling AN concentrations in working environments is very important.

The complete oxidation of AN over noble metal catalysts has been reported, but no evaluation of the formation of N_2 was carried out in these studies [10]. We previously explored catalysts that successfully convert AN into CO_2, H_2O, and N_2 rather than NO_x [6]. Ag is an efficient catalyst for AN decomposition [6]. Although Al_2O_3 is generally an effective Ag support for environmental catalysis applications, such as nitrogen oxide abatement and catalytic oxidations [11–16], TiO_2, SiO_2, and ZrO_2 are more effective supports for AN decomposition [6]. In this study, we investigated Ag catalysts supported on various materials to clarify the relationship between the AN decomposition activity and the oxidation state of Ag, as well as the role of the support material in promoting catalytic activity.

2. Experimental

2.1. Catalyst preparation

Silver catalysts supported on five kinds of metal oxide were prepared by incipient wetness impregnation. $AgNO_3$ (Wako Pure Chemical Industries) was used for the Ag precursor. The following metal oxides were used as support materials: Al_2O_3 (KHS-46; Sumitomo Chemical), SiO_2 (Wakogel C-100; Wako Pure Chemical Industries), TiO_2 (P-25; Nippon-Aerosil), ZrO_2 (RSC-H; Daiichi-Kigenso), and MgO (Nacalai Tesque). The amount of Ag loaded on the supports was adjusted to 5 wt% for each sample.

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Ag supported on ZSM-5 was prepared by ion exchange of NH_4-ZSM-5, which was prepared by ion exchange of Na-ZSM-5 (HSZ-820NAA, SiO_2/A_2O_3 molar ratio = 23.8; Tosoh) with aqueous 1 mol/L NH_4NO_3. The Ag loading was 7.4 wt%, as measured by inductively coupled plasma emission spectroscopy (Seiko Electronics; SPS 1200A).

After impregnation or ion exchange, the samples were dried at 110 °C for 12 h and then calcined at 500 °C in static air for 4 h at a ramp rate of 10 °C/min. After calcination, the catalysts were pelletized and sieved to yield granules ranging in with size from 250 to 600 µm.

2.2. Activity tests

A fixed-bed flow reactor system operated at atmospheric pressure was used to test the activity of the catalysts. Each catalyst (0.1 g) was placed in a quartz tube, and the reactant gas was flowed through the tube at a flow rate of 160 ml/min. The reactant gas was composed of He containing approximately 200 ppm AN and 5% O_2. AN vapor was produced by passing He at a predetermined flow rate through liquid AN maintained at −18 °C. Before activity measurement, the sample was pretreated by heating to 500 °C under 5% O_2 at a ramp rate of 20 °C/min and then maintaining this temperature for 1 h. The catalytic activity was measured for steady-state reactions at temperatures from 500 to 200 °C in step of 25 °C. Gas chromatography (GC) and Fourier transform infrared spectroscopy (FT-IR) were used to analyze the catalysis products. The gas chromatograph (Agilent; M200) was equipped with an MS-5A PLOT column (for H_2, N_2, CH_4, and CO analysis) and a PoraPLOT Q column (for CO_2, N_2O, and C_2–C_3 hydrocarbon analysis), as well as a thermal conductivity detector (TCD) for each column. An FT-IR spectrometer (Nicolet; Magna 560), equipped with a multi-reflection gas cell (Gemini Specialty Optics Mercury series; optical path length = 2 m) and a mercury–cadmium–telluride detector, was used for analysis of gaseous NO, NO_2, AN, and other nitrogen-containing products. FT-IR measurements were performed with a resolution of 0.5 cm^{-1}, and each spectrum was obtained by integration of 50 scans. The validity of product analysis was within 10 ppm [17]. Catalytic activity was evaluated in terms of AN conversion and product selectivity:

$$\text{AN conversion (\%)} = \frac{\text{Inlet AN (ppm)} - \text{Outlet AN (ppm)}}{\text{Inlet AN (ppm)}} \times 100,$$

$$\text{Product selectivity (\%)} = \frac{\text{N in product of interest (ppm)}}{\text{Total product N (ppm)}} \times 100.$$

To ensure reliability, the selectivities were evaluated only for AN conversion >5%.

Temperature-programmed surface reactions (TPSR) of the adsorbed AN were carried out in the same apparatus used for the activity tests. Each sample was pretreated in 5% O_2/He at 500 °C for 2 h (oxidizing conditions) or in 5% H_2/He at 400 °C for 1 h (reducing conditions). After pretreatment, the samples were cooled to 50 °C in He, and the reactant gas was flowed for 1 h over the samples at a rate of 160 ml/min, allowing AN to adsorb on the samples. The samples then were heated to 500 °C at a rate of 5 °C/min in 1% O_2/He at a flow rate of 160 ml/min.

The species present on the surface of the catalysts under the conditions used for TPSR were observed by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), using a Nicolet Nexus 870. Each sample was pretreated under oxidizing or reducing conditions as described above, and a background spectrum was obtained at room temperature in a 1% O_2/He flow. AN was then adsorbed on the sample from the flowing reactant gas at room temperature. After the sample was purged in He for 20 min, the temperature was raised at a rate of 10 °C/min in a 1% O_2/He flow. After the temperature reached a predetermined point, the sample was cooled to room temperature, and a spectrum was obtained. The spectra of adsorbed acrylamide and acrylic acid on TiO_2 also were obtained for comparison with the sample spectra. Acrylamide was adsorbed on TiO_2 by introducing the sample to its aqueous solution and then purging the solvent water with He for 1 h. Adsorption of acrylic acid was carried through the method described above for AN adsorption.

2.3. Characterization

The Brunauer–Emmett–Teller (BET) specific surface area of each sample was measured by N_2 adsorption under flow conditions (Nikkiso model 4232). X-ray powder diffraction (XRD) patterns were measured at 40 kV and 100 mA of X-ray power (Rigaku RU-300). Ag particle size was measured by means of transmission electron microscopy (TEM) using a Hitachi H-9000. Mean particle size was calculated from at least 100 Ag particles for Ag-ZSM-5, Ag/Al_2O_3, Ag/TiO_2, and Ag/SiO_2. For Ag/ZrO_2 and Ag/MgO, at least 15 Ag particles were used for calculation. The molar amount of exposed Ag was calculated from dispersion, estimated as dispersion = $1.34/d$ (nm) [18,24], where d is the mean particle size. Ultraviolet–visible (UV–vis) spectra were obtained under atmospheric conditions for fresh samples (Hitachi U-3500). $BaSO_4$ was used to obtain a background spectrum for each of the samples except for Ag/TiO_2; because TiO_2 absorbs strongly, TiO_2 powder calcined at 500 °C was used for the Ag/TiO_2 background. The sample used in AN decomposition also was measured. AN decomposition was carried out in a conventional flow reactor at 400 °C for 3 h, and then quenched with He flow. Temperature-programmed reduction by H_2 (H_2-TPR) was carried out with a temperature-programmed desorption (TPD) apparatus equipped with a TCD (Ohkura-Riken ADT700). Profiles from room temperature to 600 °C were obtained in a 100 ml/min flow of 2% H_2/Ar at a heating rate of 10 °C/min after pretreatment in a 5% O_2/He flow at 500 °C for 2 h. For comparison, a profile of Ag_2O (Wako, 99.9%) was measured. TPD of NH_3 (NH_3-TPD) was carried out with a TPD apparatus equipped with a mass spectrometer (Bel Japan TPD-1-AT). TPD profiles in the range of 100–500 °C were obtained in He at a flow rate of 50 ml/min and a heating rate of 10 °C/min after adsorption of NH_3 at 100 °C. TPD of CO_2 (CO_2-TPD) was carried out in the TPD apparatus used for the H_2-TPR tests. TPD profiles in the range of 100–500 °C were obtained in He at a flow rate of 50 ml/min and a heating rate of 10 °C/min after adsorption of CO_2 at 100 °C.

3. Results and discussion

3.1. AN decomposition activity

We previously reported the AN decomposition activity of various supported Ag catalysts [6]. Table 1 summarizes the AN de-

Table 1
Catalytic activity of supported Ag catalysts for AN decomposition.

Catalyst	T_{50} of AN conversion (°C)[a]	TOF at T_{50} (mmol/Ag-mol/s)	Maximum N_2 selectivity (%)[c]	TOF of N_2 at maximum selectivity (mmol/Ag-mol/s)
Ag-ZSM-5	433 (494)	0.86	55 (500)	0.49
Ag/Al_2O_3	383 (436)	7.8	52 (500)	3.3
Ag/TiO_2	281 (337)	4.7	87 (350)	1.9
Ag/SiO_2	274 (–[b])	16	84 (350)	6.6
Ag/ZrO_2	228 (311)	140	67 (300)	55
Ag/MgO	267 (490)	99	63 (300)	32

[a] The value in parenthesis is the activity of support.

[b] Negligible activity at whole temperatures measured.

[c] The value in parenthesis is temperature at which maximum N_2 selectivity was obtained.