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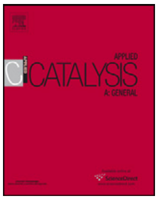

Influence of TiO_2 crystal structure on acrylonitrile decomposition over Ag/TiO_2

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ABSTRACT

The catalytic decomposition of acrylonitrile over Ag supported on different crystal phases of TiO_2 was studied. Ag/TiO_2 containing anatase TiO_2 exhibited high NH_3 and N_2 selectivity at low and high temperatures, respectively, whereas Ag/TiO_2 composed of only rutile TiO_2 exhibited medium N_2 and high NO_x selectivity at low and high temperatures, respectively. X-ray diffraction, X-ray photoelectron spectroscopy, and temperature-programmed reduction by H_2 revealed that the anatase phase favors the formation of ionic Ag, whereas the rutile phase favors that of metallic Ag. We concluded that product selectivity in acrylonitrile decomposition was influenced by the oxidation state of Ag, which was in turn affected by the crystal phase of TiO_2.

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1. Introduction

Acrylonitrile (AN) is recognized as a hazardous volatile organic compound (VOC) owing to its carcinogenicity [1]. In oxidative treatment of exhaust gases containing AN, nitrogen oxides ($NO_x = NO + NO_2$) are formed from the nitrogen atom in AN, even when thermal NO_x formation is suppressed by using a low-NO_x-emission combustor. Therefore, a catalytic purification system that can completely convert AN to harmless CO_2, H_2O, and N_2 is highly desired.

Gervasini et al. reported that Ba–Cu–Cr/Al_2O_3 combined with ozone can effectively remove AN from exhaust gases [2]. Li et al. reported that a non-noble metal catalyst mixture of La, Ce, Ni, Co, and Mn supported on Al_2O_3 showed higher activity for AN decomposition than did a noble metal catalyst mixture of Pt and Pd [3]. However, those reports focused only on AN conversion, not on product selectivity. We have reported that Ag catalysts exhibit high AN decomposition activity [4], and that this activity is greatly influenced by the type of material used to support Ag, with TiO_2 being an effective support [5]. The Ag supported on TiO_2 in our reports was composed of both metallic and oxidized species. The metallic Ag exhibited high AN oxidation activity, whereas the oxidized Ag exhibited high AN hydrolysis activity. We speculated that the reaction pathway of AN decomposition begins with hydrolysis of AN to form NH_3 over oxidized Ag, followed by NH_3 oxidation over metallic Ag. One of the controlling factors influencing these catalysts' selectivity toward N_2 formation is the ratio of oxidized and metallic Ag.

In this study, we investigated the effects of two crystal structures of TiO_2, anatase and rutile, on the chemical and physical states of Ag supported on the TiO_2. The observed TiO_2-induced changes in Ag consequently influenced product selectivity in Ag/TiO_2-catalyzed AN decomposition, as shown herein.

2. Experimental

2.1. Catalyst preparation

Ag/TiO_2 was prepared by means of incipient wetness method using $AgNO_3$ as a precursor (Wako Pure Chemical Industries), which was loaded onto the TiO_2 supports at 5 wt% Ag. Four types of TiO_2 supports were employed: anatase with a high surface area (CS-300S-12; Sakai Chemical Industry Co. Ltd., 74 m^2/g), anatase with a low surface area (Wako Pure Chemical Industries, 9 m^2/g), a mixture of anatase and rutile (P25; Nippon-Aerosil, 47 m^2/g), and rutile prepared by calcination of P25 at 900 °C for 4 h (resulting in a surface area of 5 m^2/g). We abbreviate these supports as TiO_2(HA), TiO_2(LA), TiO_2(AR), and TiO_2(R), respectively. After loading the supports with Ag, the samples were calcined at 500 °C for 4 h.

2.2. Catalyst characterization

The Brunauer–Emmett–Teller (BET) specific surface area and pore size distribution of each sample were measured by an N_2 adsorption isotherm (BEL Japan Inc., BELSORP18). X-ray powder diffraction (XRD) patterns were measured with a Rigaku RU-300

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