Catalysis Today 201 (2013) 25–31

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effect of Y-stabilized ZrO_2 as support on catalytic performance of Pt for *n*-butane oxidation

Masaaki Haneda[a,*], Magali Bonne[b,c], Daniel Duprez[b], Masakuni Ozawa[a]

[a] Ceramics Research Laboratory, Nagoya Institute of Technology, 10-6-29 Asahigaoka, Tajimi, Gifu 507-0071, Japan
[b] Laboratoire de Catalyse en Chimie Organique (LACCO), UMR 6503, CNRS – Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers, France
[c] Institut de Sciences des Matériaux de Mulhouse – IS2M, LRC-7228 CNRS, Equipe Matériaux à Porosité contrôlée, Université de Haute Alsace – ENSCMu, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France

ARTICLE INFO

Article history:
Received 10 January 2012
Received in revised form 12 March 2012
Accepted 19 March 2012
Available online 11 April 2012

Keywords:
Y-stabilized zirconium oxide
Platinum dispersion
n-Butane oxidation
Metal–support interaction

ABSTRACT

The effect of Y-stabilized ZrO_2 as support on the Pt dispersion and catalytic activity for the total oxidation of *n*-butane was investigated. From XRD, TEM and CO chemisorption measurements, Pt particles were found to be well dispersed with a size of *ca.* 10 nm over the surface of ZrO_2 and Y-stabilized ZrO_2, when Pt supported catalysts were calcined at 600 °C. Although Pt particles supported on ZrO_2 were significantly sintered by high temperature calcination above 800 °C, no aggregation of Pt particles was observed for Pt/Y–ZrO_2. When the catalyst was calcined at higher temperatures, Pt catalysts supported on Y-stabilized ZrO_2 showed higher activity than Pt/ZrO_2 for the total oxidation of *n*-butane. The intrinsic activity, expressed in terms of turnover frequency (TOF), increased with the decrease in Pt dispersion, indicating that *n*-butane oxidation over Pt catalysts supported on Y-stabilized ZrO_2 is a structure sensitive reaction. Y_2O_3 additive plays a role in improving the thermal stability of Pt particles through the metal–support interaction, while it does not alter the catalytic performance of Pt as catalytic active sites.

1. Introduction

Air pollution caused by hydrocarbons (HCs) emitted from combustors and engines is one of the most serious environmental problems because of their toxicity to human health and formation of photochemical smog [1]. A catalytic converter system is one of the most promising solutions to reduce HCs in exhaust gases. However, most HCs, especially in automotive exhaust gases, are emitted during the cold-start operation before warming up the catalytic converter [2]. Therefore, the removal of HCs at low temperature is an important issue in protecting the environment.

Supported Pt catalysts are widely employed as oxidation catalysts [3–5]. Therefore, extensive research has been undertaken to improve the activity and durability of supported Pt catalysts [6–9]. We have studied the catalytic performance of Pt catalysts supported on various metal oxides (Al_2O_3, ZrO_2, TiO_2 and H-ZSM-5) for the total oxidation of a mixture of n-decane and 1-methylnaphthalene as model hydrocarbons included in diesel exhaust to develop a highly active diesel oxidation catalyst [10,11]. We found that Pt/Al_2O_3 and Pt/ZrO_2 show high catalytic activity even after aging treatment at 750 °C for 50 h in air, and the surface density of the acidic and basic sites on Al_2O_3 seems to be one of the factors in determining the catalytic activity of Pt/Al_2O_3. Pt/Al_2O_3 with the Pt surface in the metallic state was more active than with the surface in the cationic state.

Surface acidity and basicity of metal oxide is important for controlling the dispersion state and the surface valence state of Pt particles. For example, Nagai et al. [12] reported that Pt in Pt/ceria-based oxide does not sinter after aging treatment at 800 °C in air because of the formation of Pt—O—Ce bonds (*i.e.*, the Pt-oxide-support interaction) which act as an anchor for Pt particles on ceria-based oxides. They also found that particle size of Pt supported on various oxides after aging decreases with the increase in the electron density of oxygen, which corresponds to basicity, in the oxide support. Yoshida et al. [7,13] investigated the valence state of Pt supported on various metal oxides by Pt L_{II}- and L_{III}-edge XANES, and found that Pt on the acidic support materials was less oxidized than that on the basic support material in the oxidizing atmosphere. Therefore, the modification of metal oxide to control the surface acidity and basicity is key technology for improving the performance of supported Pt catalysts.

In the present study, Y-stabilized ZrO_2 was employed as support for Pt catalysts. Since Y_2O_3 is a metal oxide whose surface exhibits basic properties [14], the surface acidity and basicity of ZrO_2 are expected to be modified by introducing Y as the dopant. In addition, the thermal stability of ZrO_2 can be improved by Y additive

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* Corresponding author. Tel.: +81 572 27 9964; fax: +81 572 27 6812.
E-mail address: haneda.masaaki@nitech.ac.jp (M. Haneda).

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http://dx.doi.org/10.1016/j.cattod.2012.03.025

[15], resulting in sintering inhibition of Pt. We investigated the effect of Y-modification of ZrO_2 on the catalytic performance of Pt for the total oxidation of *n*-butane. Our interest in the use of *n*-butane oxidation comes from the fact that *n*-butane is one of the non-combustible saturated hydrocarbons included in automotive exhaust and thus *n*-butane oxidation has attracted attention [16–21]. Various catalyst characterizations were performed to examine the possible factors directly affecting the catalytic performance of Pt catalyst supported on Y-stabilized ZrO_2.

2. Experimental

2.1. Catalyst preparation

ZrO_2 (TZ-0, $14\,m^2\,g^{-1}$) and Y-stabilized ZrO_2 (Y–ZrO_2) with different Y contents (TZ–2Y, Y = 2 mol.%, $16\,m^2\,g^{-1}$ and TZ–8Y, Y = 8 mol.%, $16\,m^2\,g^{-1}$) supplied from Tosoh Corporation were used as the support for catalyst preparation. Pt/ZrO_2 and Pt/Y–ZrO_2 catalysts were prepared by impregnation of ZrO_2 and Y-stabilized ZrO_2 with a solution of $Pt(NO_2)_2(NH_3)_2$ (Tanaka Precious Metals, Pt concentration = 4.595 wt.%), respectively, followed by drying and calcination at 500 °C for 5 h in air. Catalyst samples were further calcined at 600, 700, 800 and 900 °C for 5 h in air. The loading of Pt was fixed at 1 wt.%. The samples are expressed as Pt/ZrO_2-*x* or Pt/*n*Y–ZrO_2-*x*, where *x* and *n* are the catalyst calcination temperature and the Y content, respectively.

2.2. Activity tests

The catalytic activity was evaluated using a fixed-bed continuous flow reactor. A reaction gas mixture containing *n*-C_4H_{10} (2000 ppmC) and O_2 (5%) diluted in He as the balance gas was fed through a catalyst (0.1 g) that had been pretreated *in situ* in a flow of 5% H_2/He at 400 °C for 1 h at a rate of $100\,cm^3\,min^{-1}$. The activity was measured while increasing the temperature from 100 to 600 °C at a rate of $5\,°C\,min^{-1}$. The effluent gas was analyzed by an online gas chromatograph (Shimadzu GC-2014ATF) equipped with a Molecular Sieve 13X column (for the analysis of O_2 and CO), a Porapak QS column (for the analysis of CO_2) and 25% DC-200 on a Shimalite column (for the analysis of *n*-C_4H_{10}). In the present study, no formation of CO was observed.

2.3. Catalyst characterization

The crystal structure of the samples was identified by XRD (Rigaku MiniFlexII) measurements using Cu Kα radiation at 30 kV and 15 mA. The dispersion of Pt, defined as the ratio of $Pt_{surface}$ over Pt_{total}, was estimated by CO chemisorption at room temperature using a dynamic pulse adsorption apparatus (Ohkura Riken, BP-1), where the sample was first reduced with H_2 at 400 °C for 1 h and then cooled to room temperature in flowing He. Direct observation of Pt particles by TEM was performed with a JEM-2100 (JEOL) operating at an acceleration voltage of 200 kV.

FT-IR spectra of adsorbed CO, as a probe molecule, were taken with a Nicolet 6700 FT-IR spectrometer at a resolution of $4\,cm^{-1}$ in a flow of 0.5% CO/He at 50 °C, where a self-supporting sample disk of about $14\,mg\,cm^{-2}$ placed in an IR cell with CaF_2 windows was pretreated at 400 °C in a flow of 5% H_2/He and then cooled to 50 °C in flowing He.

Temperature-programmed desorption of ammonia (NH_3-TPD) and CO_2 (CO_2-TPD) was performed using a BELCAT (Bel Japan Inc.) to estimate the acidity and basicity of the supports, respectively. Each catalyst sample was pretreated in a flow of He at 600 °C. After cooling to 100 °C in flowing He, ammonia adsorption was carried out by passing a gas mixture of 0.5% NH_3/He through the sample bed at 100 °C for 1 h. On the other hand, CO_2 adsorption was carried out by passing a gas mixture of 0.5% CO_2/He through the sample bed at 50 °C for 1 h. After the adsorption gas was purged with He to remove physically adsorbed ammonia and CO_2 at each adsorption temperature, NH_3-TPD and CO_2-TPD measurements were carried out up to 600 °C at a heating rate of $10\,°C\,min^{-1}$ in flowing He at a flow rate of $60\,cm^3\,min^{-1}$. A quadrupole mass spectrometer (M-201QA-TDM, Canon Anelva) was used to analyze the desorbed ammonia and CO_2.

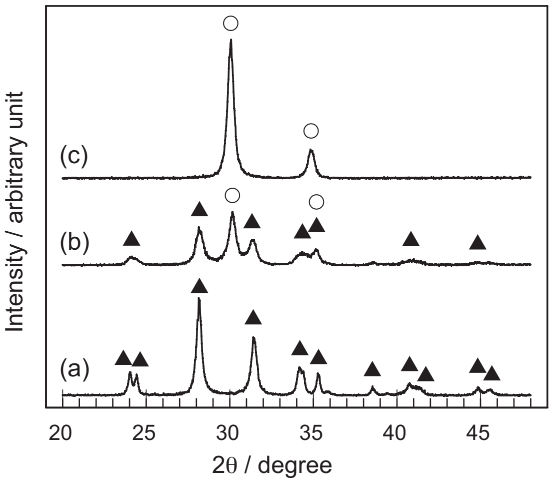

Fig. 1. XRD patterns of (a) ZrO_2, (b) 2Y–ZrO_2 and (c) 8Y–ZrO_2: (▲) for ZrO_2 (monoclinic) and (○) for ZrO_2 (tetragonal and/or cubic).

3. Results and discussion

3.1. Physical properties of support

Fig. 1 shows the XRD patterns of ZrO_2 and Y–ZrO_2 with different Y contents. It appears that the crystal phase of ZrO_2 is totally different depending on the Y content. ZrO_2 showed distinct XRD peaks indexed to a monoclinic phase (Fig. 1(a)). In accordance with previous reports [22,23], 8Y–ZrO_2 exhibited a cubic phase (Fig. 1(c)). This suggests the formation of Y_2O_3–ZrO_2 solid solution in which Y^{3+} ions are completely incorporated into the ZrO_2 lattice. On the other hand, 2Y–ZrO_2 was found to have a mixture of monoclinic and tetragonal phases (Fig. 1(b)), suggesting the coexistence of thermodynamically metastable and stable phases.

Ii et al. [24] reported that Y cations in 3 mol.% Y-stabilized ZrO_2 (TZ–3Y) segregate to the surface of the tetragonal particle. This leads us to consider that the surface properties of ZrO_2 are significantly different depending on the Y content. The surface acidity and basicity of Y_2O_3–ZrO_2 composite oxides have been studied by many researchers. For example, Li et al. [25] reported that the amount of acidic and basic sites largely decreased when 2.5 mol.% Y_2O_3 was doped into ZrO_2 compared with that over pure ZrO_2. Further increase in Y_2O_3 content slightly increased the amount of acidic sites while decreasing the amount of basic sites. On the other hand, Viinikainen et al. [26] reported that the total amount and strength of both acidic and basic sites on 5 mol.% Y_2O_3–ZrO_2 is larger than that on ZrO_2. The surface acidity and basicity of Y_2O_3–ZrO_2 composite oxides could be dependent on various factors such as Y content, crystal structure, crystallinity and so forth.

In order to evaluate the surface acidity and basicity of ZrO_2 and Y–ZrO_2 with different Y contents, NH_3-TPD and CO_2-TPD measurements were carried out, respectively. Fig. 2 shows the NH_3-TPD profiles of ZrO_2 and Y–ZrO_2. ZrO_2 gave two broad NH_3 desorption peaks at 185 and 310 °C (Fig. 2(a)). When 2 mol.% Y_2O_3 was added into ZrO_2 (Fig. 2(b)), a slight increase in the amount of NH_3 desorption at 310 °C and a slight shift of desorption peak to a higher