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Surface structure of yttrium-modified ceria catalysts and reaction pathways from ethanol to propene



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ABSTRACT

The additive effect of 31 metals on activity of ceria catalysts was studied for the conversion of ethanol to propene. Yttrium gave the best results and the propene yield showed a volcano-shaped dependence on the Y amount, being maximized at 20 atom% Y to that of Ce. The catalyst was stable due to very small carbon deposition rate which was approximately 1/100 of that on the parent CeO₂ catalyst. The water addition increased the propene yield to 30%, decreased the ethene yield to 37%, and did not change the durability. The physicochemical characterization of the Y/CeO₂ catalysts indicated that the surface of active catalysts was covered with a solid solution of CeO₂ and Y₂O₃. Pulse experiments of various candidate compounds suggested that the reaction pathways were ethanol \rightarrow acetaldehyde \rightarrow ethyl acetate \rightarrow acetic acid \rightarrow acetone \rightarrow 2-propanol \rightarrow propene through Tishchenko reaction, ketonization, and Meerwein–Ponndorf–Verley reduction.

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1. Introduction

Propene is one of the most important ingredients in petroleum chemistry and its needs continuously increase because of growing production of propene derivatives, such as polypropene, propene oxide, and acetonitrile [1]. Today, propene is produced through hydrothermal cracking of naphtha. Depletion in fossil fuel and increased concerns on the environment stimulate replacing petroleum with renewable resources. Several researchers including us have suggested that bioethanol is a promising renewable platform chemical to yield various C3 and C4 compounds [2–13]. The present study was thus devoted to the conversion of ethanol to propene.

Zeolite catalysts are well known to show 20-30% of propene yield, except for short-term high yields, but this selectivity decreased with duration [14–17]. Oligomerization, cracking, and aromatization proceed on the acid sites of the zeolite pore, and propene is selectively produced as a result of shape selectivity of the pore window. Such uncontrolled reactions, however, result in coke formation and short lifetimes of catalysts. On the other hand, Ni-ion-loaded MCM-41 [8] and Sc-modified In₂O₃ catalysts [9,10] offered new types of catalysis for the production of propene without shape selectivity, but the catalytic activity gradually decreased with duration at 30 vol% of ethanol (the high

concentration of ethanol is essential to reduce running costs of the industrial processes). Therefore, new catalysts workable under the practical conditions are needed to produce propene from bioethanol.

Various metal oxide-based catalysts have been examined as catalysts for the conversion of ethanol, but most of the products besides ethene are oxygenated compounds, such as aldehydes, ketones, and higher alcohols [2–7,18–21]. Our attention was paid to the selective conversion of C_x -alcohol to C_{2x-1} -ketone on ceriabased catalysts [2–6] and assumed that any acetone formed could be hydrogenated and subsequently dehydrated by controlling the acid-base and redox properties of catalysts. Indeed, yttrium-loaded CeO₂ was found by us to show the stable catalytic activity for the selective conversion of ethanol to propene [12]. In this study, we first examined the additive effect of 31 metals on the ceria catalysts in the absence and presence of water. Niobium and yttrium were then selected as effective additives and the dependences of activity on their added amounts were studied. Second, effect of the preparation method was examined for the better catalyst, Y/ CeO₂. The structural, redox, and acid-base properties of Y/CeO₂ were characterized to reveal the correlation between the catalytic activity and the properties. Last, the reaction pathways were discussed on the basis of the results of product distributions in the continuous flow and pulse reactions.



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2. Experimental

2.1. Preparation of metal-modified ceria catalysts

Ceria-based catalysts were prepared using a conventional impregnation method or a co-precipitation method. In the former, the parent ceria, obtained from Catalysis Society of Japan (JRC-CEO-3, 85 m² g⁻¹), was impregnated using aqueous solutions of the metal salts: nitrates of Li, Mg, Ca, Y, La, Sm, Er, Mn, Fe, Co, Ni, Cu, Zn, Rh, Cd, Al, In, and Bi, acetates of Sc and Sn, ammonium salts of Ti, V, Nb, Mo, W, and Re, alkoxides of Ta and Si, and chloride of Ir. In the latter, Ce(NO₃)₃·6H₂O, Y(NO₃)₃·6H₂O, and ammonium hydrogen carbonate were used as precursors and a precipitant, respectively, and the solid solution was prepared according to the literature [22]. All samples were calcined at 873 K for 5 h in air. Catalysts prepared by the impregnation and the co-precipitation method are denoted by $M(x)/CeO_2$ and M(x)-CeO₂, respectively, where M and *x* represent the metal used and the atomic % to that of Ce.

2.2. Measurement of catalytic activity

Ethanol (>99.5%, Kanto chemical) was used without further purification. The continuous flow reactions were conducted in a fixed-bed plug-flow reactor made of guartz (i.d. 10 mm) at an atmospheric pressure under the following conditions: catalyst weight 0.05–2.0 g (particle diameter, 300–600 μ m), total flow rate 12–32 ml min⁻¹, partial pressure of ethanol (P_{FtOH}) 30 vol%, P_{H2O} 0-30 vol%, N₂ balance. Before the catalytic runs, the catalysts were heated in a N₂ flow at 673 K for 1 h. The products were analyzed with an online automatic gas chromatograph (AG-1, Round Science) equipped with four kinds of packed columns: (1) activated charcoal, (2) MS 5A, (3) Porapak Q, and (4) PEG-20 M. The columns 1-3 were independently connected to the three TCD detectors to determine the yields of ethene, CO, and CO₂. The column 4 was connected to the FID detector to determine the yields of other carbon products. The C4-C7 hydrocarbons and oxygenated products were analyzed as needed with an offline FID gas chromatograph (GC-2014, Shimadzu) with a capillary column of CP-7561 (10 m, Varian) or GS-Q (30 m, Agilent). Conversion levels of ethanol and yields of carbon products ($C_n H_x O_v$, *n* = carbon number) were calculated by Eqs. (1) and (2), where the partial pressures of ethanol before and after the reaction are denoted by P_{EtOH} and P'_{FtOH} , respectively.

Ethanol conv.
$$(\%) = 100(1 - (P'_{EtOH}/P_{EtOH})(P_{N2}/P'_{N2}))$$
 (1)

$$C_{n} \text{ Yield } (\%) = 100(n P_{Cn}^{\prime}/2P_{EtOH})(P_{N2}/P_{N2}^{\prime})$$
(2)

For pulse experiments, ethyl acetate (>99.5%, Kanto chemical), acetic acid (>99.5%, Kanto chemical), acetone (>99.9%, Aldrich), and ethanol (>99.5%, Kanto chemical) were used as substrates without further purification. Each substrate with volume of 2 μ l was fed into the catalyst bed in the quartz glass reactor (i.d. 7.6 mm) at 403 K under the following conditions: catalyst weight 0.1 g (particle diameter, 300–600 μ m), total flow rate 10-80 ml min⁻¹, N₂ balance. As needed, ethanol, water, or H₂ gas was used as a co-reactant. The pretreatment and the product analysis methods were the same as those for the continuous flow reactions.

2.3. Characterization

 N_2 adsorption isotherms were determined at 77 K with an automatic gas sorption meter BEL Japan Belsorp mini II. Before the measurements, the samples were degassed at 423 K for 2 h in

vacuum. Field-emission scanning electron microscopy, FE-SEM, images were collected with a Hitachi HR-S5500. Powder X-ray diffraction, PXRD, patterns were measured using a Rigaku Ultima IV diffractometer with monochromated Cu Ka radiation $(\lambda = 0.15418 \text{ nm}, 40 \text{ kV},$ 40 mA). Temperature-programmed reduction with hydrogen, H₂-TPR, profiles were recorded with a BEL Japan BelCat. X-ray photoelectron (XP) spectra were measured with an Omicron EA125 XPS system. All binding energies were corrected using the values of C 1s (285.0 eV). X-ray absorption fine structure, XAFS, analysis was carried out at the BL-9C station of the Photon Factory at the High Energy Accelerator Research Organization, Japan. The energy and current of electrons in the storage ring were 2.5 GeV and 350 mA, respectively. Energy calibration was performed using a Cu foil (8.9788 keV). Prior to the measurements, the samples were evacuated at 673 K. Data analysis was performed using the REX2000 program (Ver. 2.5.9, Rigaku). The k^3 -weighted extended X-ray absorption fine structure. EXAFS, oscillation was Fourier-transformed (FT) into the r space using the k range of 3.0–14.0 Å⁻¹ for Y or 3.0–10.0 Å⁻¹ for Ce. Curve fitting analysis was carried out in the *r* range 1.2–2.2 Å for the Y–O contribution or 1.5–2.3 Å for the Ce–O to calculate the average nearest neighbor coordination number and the average bond lengths of Y-O and Ce-O. Backscattering amplitudes and phase-shift functions were calculated from the crystal structures of Y₂O₃ and CeO₂ using the FEFF6 code.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were measured in a DR-600Bi diffuse reflectance cell using Jasco FTIR-6300 spectrometer equipped with a MCT detector. Selfsupported KBr plates were used as windows for the cells. Scan times and a resolution were 32 and 4 cm⁻¹, respectively. The KBr powder evacuated at 303 K was used as a reference. Prior to the measurements, the sample was evacuated at 673 K for 1 h. Pyridine (>99.5%, Wako) or CO₂ (>99%, GL Sciences) was introduced onto the sample at 303 K for 5 min and then evacuated at the same temperature for 30 min. All spectra were recorded as the difference spectra before and after the introduction of adsorbates.

3. Results and discussion

3.1. Additive effect of metals on activity of ceria catalysts

Table 1 summarizes the activity of various ceria catalysts modified with mainly 10 atom% metal additives, in which the data after 0.75 h are shown because the activity was often changed with duration. The metals were listed in the sequence of the family. The surface areas of M(10)/CeO₂ are also summarized in the table and were roughly constant at 52–61 m² g⁻¹ independent of the metal additives.

The conversion degrees of ethanol were all 80–100% under the present reaction conditions. Among 31 metals, the addition of Y, Sm, Ti, Nb, or Ta increased the propene yield, while that of Fe, Co, Cu, Zn, Sn, or Bi increased the acetone yield. The formation of acetone on the latter group was well consistent with the previous reports on ZnO- and CeO₂-based catalysts [2-6] that were active for the conversions of C_x -alcohols to C_{2x-1} ketones. As shown in Run 18 of Table 1, the Nb(10)/CeO₂ catalyst exhibited the highest propene vield of 32%, but its activity was not stable. The deactivation with duration was also observed on the Ti- or Ta-modified CeO₂ catalyst. In contrast, the Y(10)/CeO₂ catalyst showed no deactivation during continuous service of 80 h, although the propene yield, 19% (Run 6), was lower than those on the Nb(10)/CeO₂ and the $Ti(10)/CeO_2$. Based on the high propene yield or the long life, the Nb- and Y-modified ceria were selected as the catalysts in the subsequent detailed study.

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