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Yttrium-Modified Ceria As a Highly Durable Catalyst for the Selective Conversion of Ethanol to Propene and Ethene

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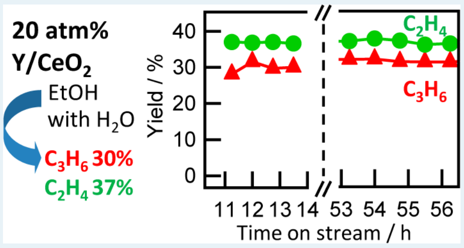
Supporting Information

ABSTRACT: Among 31 CeO_2-based catalysts modified with various additives, those doped with yttrium showed the most stable activity for the conversion of ethanol to propene and ethene. The yields of propene and ethene were 25 and 50%, respectively, at 693−703 K in the absence of water and did not change after continuous catalysis over 80 h. The carbon deposition rate on the catalyst was ~1/100 of that reported for zeolite catalysts. The addition of water into the reaction system increased the propene yield to 30% and decreased the ethene yield to 37%.



KEYWORDS: *ceria, yttrium, bioethanol, heterogeneous catalysis, biomass conversion*

Conversion of biomass-derived feedstock to chemicals has been an important research goal to reduce the amount of fossil fuels used. Bioethanol is recognized as a promising alternative to petroleum because of its wide availability and potential for further production of various chemicals.[1] Propene and ethene are essential building blocks for chemicals and polymers; in particular, the former is in high demand as a result of the growing production of propene derivatives, such as polypropene, propene oxide, acrylonitrile, etc.[2] The conversion of ethanol has been widely studied on acidic zeolites and metal oxides;[3−25] however, the lifetimes of these catalysts are insufficient.

With zeolites, the selectivity for propene was 20−30%, except for short-term high yields, but this selectivity decreased with increasing reaction time.[3−9] It is widely accepted that many reactions, such as oligomerization, cracking, and aromatization, occur on the acidic sites of the zeolite pores, and ethene and propene (and butenes) are selectively released from the pores due to shape selectivity. However, random reactions in the pores result in coke formation and short lifetimes for catalysts. Very recently, the conversion of ethanol to propene was reported on nickel ion-loaded mesoporous silica MCM-41 (Ni-M41)[23] and Sc-loaded In_2O_3.[24] Although these oxide catalysts produced new types of catalysis for the production of propene without shape selectivity, the catalytic activity gradually decreased with the reaction time at 30 vol % of ethanol (the high concentration of ethanol was required to reduce running costs of the practical process). The decrease in the activity of Ni-M41 was not improved by addition of water, and the activity of Sc/In_2O_3 became stabilized in the presence of water.[24] Currently, catalysts that are stable in the absence of water have been required to achieve the effective catalytic conversion of ethanol to lower olefins.

Various neutral and acid−base oxides have been examined for conversion of ethanol to related substances.[11−25] In addition to ethene, the major products reported were oxygenated compounds, such as aldehydes and ketones.[11−20] We focused on the selective formation of C_{2x-1}-ketone from C_x-alcohol using metal oxide catalysts[11−20] and assumed that any acetone formed could be hydrogenated and subsequently dehydrated by controlling the acid−base and redox properties. On the basis of the conversion of 1-propanol to 3-pentanone on Fe_2O_3−CeO_2,[18,20] the present study was devoted to investigating the activity of various metal ion-modified ceria catalysts. Y-doped ceria was found to show a very stable catalytic activity at 30 vol % of ethanol, even without the addition of water. The introduction of water did not impair the stability but improved the selectivity to propene. The Y/CeO_2 catalyst would be a strong candidate for the selective conversion of ethanol to propene and ethene.

The parent CeO_2 was supplied by the Catalysis Society of Japan (JRC-CEO-3, 85 $m^2\ g^{-1}$), and metal nitrates or acetates were employed as precursors for the preparation of the modified catalysts. Thirty-one metal-modified ceria catalysts (denoted by $M(x)/CeO_2$, where M is the metal added, and x is the atom % of M to Ce), were prepared by a conventional impregnation method, except for Fe/CeO_2 and Zr/CeO_2, which were prepared by a citric acid method.[18] All samples were calcined at 873 K for 5 h in air. The resulting catalysts exhibited 50−59 $m^2\ g^{-1}$ of BET surface areas. Details about the catalytic activity measurements are described in the Supporting Information.

Table S1 (Supporting Information) summarizes the effect of the 31 types of metal additives on the catalytic activity of the ceria-based catalysts. Selected results are shown in Figure 1, where the yields of the products after 0.75 h are plotted as the bars on the left and those after 3 h as the bars on the right. The parent CeO_2 showed 12 and 31% yields of propene and ethene,

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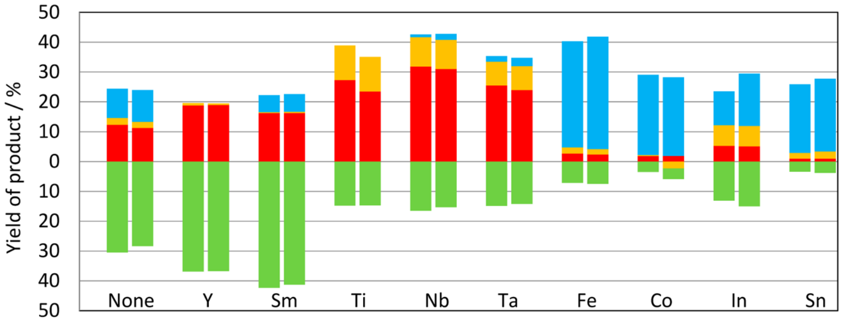

Figure 1. Change in the catalytic activity of ceria with the addition of 20 (Fe) or 10 atom % (metals other than Fe) metal. The right and left bars show the product yields after 0.75 and 3 h, respectively. The yield of ethene (green), propene (red), butenes (orange), and acetone (blue) are shown. Reaction conditions: catalyst weight, 2.0 g; total flow rate, 12.8 mL/min; P_{EtOH}, 30 vol%; N_2 balance; and reaction temp, 673−723 K.

respectively, after 0.75 h. The addition of Y, Sm, Ti, Nb, or Ta increased the propene yield and decreased the amount of acetone. In contrast, the addition of Fe, Co, In, or Sn decreased the propene yield and increased the acetone yield. The oxides of the latter group were very similar to those that were active in the formation of 3-pentanone from 1-propanol,[18,20] indicating the analogous catalysis for the two substrates to the ketones. Nb(10)/CeO_2 gave the highest propene yield of 32% (Figure 1 and run 19 in Supporting Information Table S1) but gradually lost activity with increasing reaction times; the yields were 31 and 23% after 3 and 19 h.

The TG-DTA analysis of the Nb(10)/CeO_2 catalyst after the reaction indicated a carbon deposition of 4.8 wt % (Supporting Information Figure S1-A and entry 2 in Supporting Information Table S2). The average deposition rate of carbon on the catalyst was calculated to be ~2.2 $\mathrm{mg_{carbon}\ g_{cat}^{-1}\ h^{-1}}$. This rate is roughly comparable to those reported for zeolite catalysts (entries 3−6 in Supporting Information Table S2). Deactivation of Nb(10)/CeO_2 would result from carbon deposition. Similar behavior was observed on the Ti- and Ta-loaded CeO_2 catalyst. In contrast, the Y(10)/CeO_2 catalyst showed no deactivation during continued catalytic use, although the propene yield was 19%, which was smaller than those on Nb/CeO_2 and others. The Y-modified ceria was therefore selected as a potentially durable catalyst for the conversion of ethanol to propene and ethene. The catalytic activity of Y/CeO_2 was investigated in more detail with regard to the Y content and the reaction conditions.

First, the results obtained in the absence of water will be discussed. Figure 2 shows the effect of the amount of loaded yttrium on the catalytic activity. The yields of both propene and ethene increased with increasing Y loading, were maximized at 20 atom %, and then decreased. It would be worth noting that the activity of pure Y_2O_3 was not high, as shown in run 39 in Supporting Information Table S1. The maximum yields of propene and ethene on Y(20)/CeO_2 were 25 and 52%, respectively, at 703 K (run 9 in Supporting Information Table S1). In contrast, the yields of acetone and butenes decreased to 0−1% with increasing Y loading. The amounts of CO, CO_2, and methane produced on Y(20)/CeO_2 were 2, 8, and 2%, respectively. Acetaldehyde was not detected. The total yields of the products were always ~90% (carbon basis), which were not consistent with 100% conversion of ethanol. Because the carbon deposition rate was very low on Y(20)/CeO_2, as will be shown below, the discrepancy of the conversion of EtOH with the total yield of the products is likely the result of the formation of products such as carboxylic acids and esters. Their production was, indeed, confirmed by an off-line capillary GC system, but the quantitative analyses were not carried out because of too long intervals of the analyses.

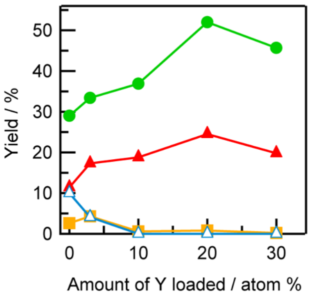

Figure 2. Catalytic activity of Y-doped ceria as a function of the amount of Y loaded for the production of ethene (green circle), propene (red triangle), butenes (orange square), and acetone (blue triangle). Reaction conditions: catalyst weight, 2.0 g; total flow rate, 12.8 mL/min; P_{EtOH}, 30 vol %; and reaction temp, 693−723 K.

Next, long-term stability of Y(20)/CeO_2 was investigated in the absence of water. Figure 3A shows the yields of propene and ethene at 693 K as a function of reaction time. The yields of propene and ethene were almost constant at 25 and 49% during a continuous experiment 80 h in length. Y/CeO_2 was shown to be a durable catalyst for the production of propene in the absence of water. As shown in Supporting Information Figure S1-C and Table S2, entry 1, the amount of carbon deposited on Y(20)/CeO_2 and the deposition rate were 0.16 wt % and 0.02 $\mathrm{mg_{carbon}\ g_{cat}^{-1}\ h^{-1}}$, respectively. The latter value was 1/100 of those using zeolite catalysts (entry 1 against entries 3−6, Supporting Information Table S2).

It is well-known that coarsely distilled bioethanol usually contains 5−10 wt % water as liquid; therefore, the effect of the addition of water (30 vol%) into the reaction system was examined. The results are depicted in Figure 3B. The propene yield increased to 30%, while that of ethene decreased to 37%. The stability of the catalytic activity of Y(20)/CeO_2 was maintained in the presence of water. The fact that water addition is not preferred for zeolite catalysts, resulting from dealumination from the lattice, could favor the Y(20)/CeO_2 catalyst for the practical application in ethanol chemistry.

Supporting Information Figure S2 shows the X-ray diffraction patterns of the Y/CeO_2 catalysts. All samples gave diffraction patterns assignable only to the cubic fluorite structure of CeO_2 (JCPDS No. 34-394, 0.5410 nm). Supporting Information Figure S3 represents the EXAFS spectra of the Y/CeO_2 catalysts together with those of Y_2O_3

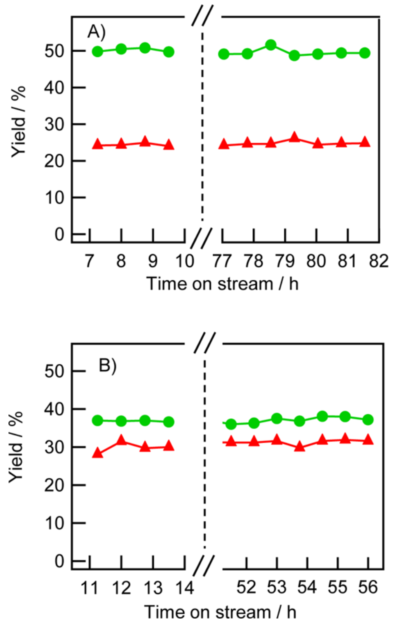

Figure 3. Long-term experiments of the catalytic activity of Y(20)/CeO_2 for the production of ethene (green circle) and propene (red triangle) in the absence (A) and presence (B) of water. Reaction conditions: catalyst weight, 2.0 g; total flow rate, 12.8 mL/min; P_{EtOH}, 30 vol %; P_{H2O}, 0 (A) and 30 vol % (B); reaction temp, 693 (A) and 703 K (B).

and a Y_2O_3−CeO_2 solid solution prepared by a coprecipitation.[26] The spectrum of Y(20)/CeO_2 was very similar to that of the solid solution, indicating the formation of a Y_2O_3−CeO_2 solid solution on the Y(20)/CeO_2 sample, which agrees with the previous characterization.[26−28] The solid solution phase should be catalytically active, although more detailed characterization should be carried out.

Finally, the possible reaction pathways and the effect of water vapor addition on the present catalysis will be briefly discussed, although more detailed reaction results (for example, the dependencies on the contact time and the partial pressure of ethanol and the reactivity of the possible intermediates) should be presented. In general, the dehydration of alcohols to olefins is promoted by acidic catalysis, and the dehydrogenation to aldehydes is promoted by basic catalysis.[10−18] The conversions of aldehydes to ketones and ketones to olefins are widely reported. Taking into account the suggested pathways on various metal oxides,[10−25] including Sc/In_2O_3[24] and $Zn_xZr_yO_z$,[25] the reaction on the Y/CeO_2 catalyst would proceed in the following manner: ethanol → ethene and ethanol → acetaldehyde → acetone → propene. In the latter pathway, acetaldehyde would be converted to acetone through the aldol reaction, the Tishchenko reaction, or direct acetic acid formation and subsequent ketonization. With respect to the effect of water addition, the dehydration of ethanol on acid sites is reported to be inhibited by adsorption of water.[7,9] This might result in the change in the yields of propene and ethene in the presence of water. The reaction mechanism will be elucidated in the near future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of experimental procedures, results of activity measurement, TG-DTA, XRD, and Y−K EXAFS. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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