Editor's Choice

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One-path and Selective Conversion of Ethanol to Propene on Scandium-modified Indium Oxide Catalysts

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The direct and stable conversion of ethanol to propene with yields up to 60 mol % was achieved on scandium-modified indium oxide catalysts at 823 K in the presence of water and hydrogen. The reaction pathways are also suggested, ethanol → acetaldehyde → acetone → propene, which is quite different from those on zeolites and on nickel ion-loaded silica catalysts.

The use of bio-ethanol (*b*EtOH) as automobile fuels has increased rapidly over the world with expanded availability and reduced cost.[1–3] The conversion of this particular biomass-based feedstock to highly valuable chemicals has also been an important research goal.[4–7] Direct conversion to propene and isobutene has very recently been reported on nickel ion-loaded mesoporous silica Ni-MCM-41 (Ni-M41)[8] and also a mixed oxide $Zn_1Zr_{10}O_z$.[9] Propene production is notably desirable, due to the increasing demand for propene derivatives such as propene oxide, acrylonitrile, and polypropene. Catalytic conversion of EtOH on zeolites has widely been reported, but the selectivity toward propene was approximately 20–30% and decreased with reaction time.[10] Various oligomerization and scission reactions on strong acid sites in the zeolite pores lead to ethene, propene, and butenes due to the shape selectivity of pore windows. However, reactions in the pores eventually result in coke formation and short lifetimes of catalysts. On the other hand, Ni-M41 was active for the propene synthesis through dehydration, dimerization, isomerization, and metathesis.[8,11] Our additional experiments on the Ni-M41 process indicated deactivation of Ni-M41 at 30 vol % of ethanol during practical application. New catalyst(s) usable under practical conditions, therefore, should be developed to produce biochemicals and bioplastics from bio-ethanol.

Our attention was focused on the formation of ketones from alcohols in which C_x-alcohols are converted into C_{2x-1}-ketones; for example, ethanol to acetone on $ZnO–Fe_2O_3$ etc.[7,12,13] and 1-propanol to 3-pentanone on $CeO_2–Fe_2O_3$.[14] It is expected that mixed oxide catalysts with hydrogenation–dehydration activity for acetone (Reaction 3) could directly convert ethanol to propene (Reaction 4), though there has been no report on direct conversion through the suggested pathways.

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2 \tag{1}$$

$$CH_3CHO + CH_3CH_2OH + H_2O \rightarrow CH_3COCH_3 + CO_2 + 3H_2 \tag{2}$$

$$CH_3COCH_3 + H_2 \rightarrow CH_2{=}CHCH_3 + H_2O \tag{3}$$

$$2CH_3CH_2OH \rightarrow CH_2{=}CHCH_3 + CO_2 + 3H_2 \tag{4}$$

Our study revealed that In_2O_3-based oxides were notably active for the direct conversion of ethanol to propene, and the propene yield reached approximately 60% at 30% partial pressure of ethanol. The reaction pathways were also suggested based on the change in the products.

Indium oxide, In_2O_3 ($4.2\,m^2\,g^{-1}$ after calcination at 1073 K for 5 h), was commercially obtained from Kanto Chemical Co. Japan. Metal-loaded In_2O_3 samples were prepared by a conventional impregnation method using mainly nitrate salts. Metal loadings were determined by inductively coupled plasma analysis after the samples were dissolved in HF solutions. All catalysts were calcined at 1023 K for 5 h, and the respective particle sizes were adjusted to 300–600 μm for use in catalytic runs. The structure of the resulting metal-loaded In_2O_3 was confirmed by X-ray diffraction analysis. The catalytic reaction was carried out using a fixed-bed flow reactor at an atmospheric pressure. The catalyst was loaded into the reactor made of quartz, heated in N_2 at 673 K, and EtOH ($P_{EtOH} = 30\%$, others, and N_2 balance) was subsequently let into the reactor at the desired temperature using a mass flow controller for liquid. The product distribution was determined by an online gas chromatograph. The yield and selectivity were calculated on the basis of carbon.

The catalytic activity of the parent In_2O_3 was studied using a fixed-bed flow reactor at atmospheric pressure as a function of temperature and reaction time. The results are summarized in Figure 1 and Table 1. The conversion degrees of EtOH were 94–100% at 623–823 K. The major by-products were ethene, butenes (mostly isobutene), acetone, and acetaldehyde. In the comparison of the initial activity at each temperature, the yield of propene was maximized at 723 K. Above 773 K, the yield decreased, while yields of acetone and acetaldehyde increased. Additionally, the yield of propene at 723–823 K greatly diminished as the reaction time increased. In contrast, the acetone yield gradually increased at 723–773 K and subsequently decreased at 823 K with reaction time, while the acetaldehyde yield significantly increased at 823 K. The results suggest that the incipient stage of deactivation made the catalysis for Reaction 3 weak and that further deactivation caused the lower activity for Reaction 2. Therefore, only Reaction 1 progressed. The apparent changes in the catalysts before and after the reaction were the reduction of In_2O_3 to indium metal and the accumulation of carbon on the catalyst. The former is depicted in Figure 2, which shows XRD patterns of indium metal after reaction.

The effect of various metals in the In_2O_3 was examined to improve the stability and enhance the activity. Table 1 summarizes mainly the results at 773 K after 45 min with 10 atom % metal additive. The metals are listed in the order of family of elements. Among 28 kinds of metals, the addition of Sc, Zr, V, Cr, Mo, Co, Ni, and Cu increased propene production, while Li, K, Ca, Ba, Y, La, Ce, Ti, Fe, Al, Sn, and Sb increased the acetone yield. The addition of Er, Nb, W, Mn, Pd, Zn, Ga, and Bi had no effect on propene or acetone production. Acid–base

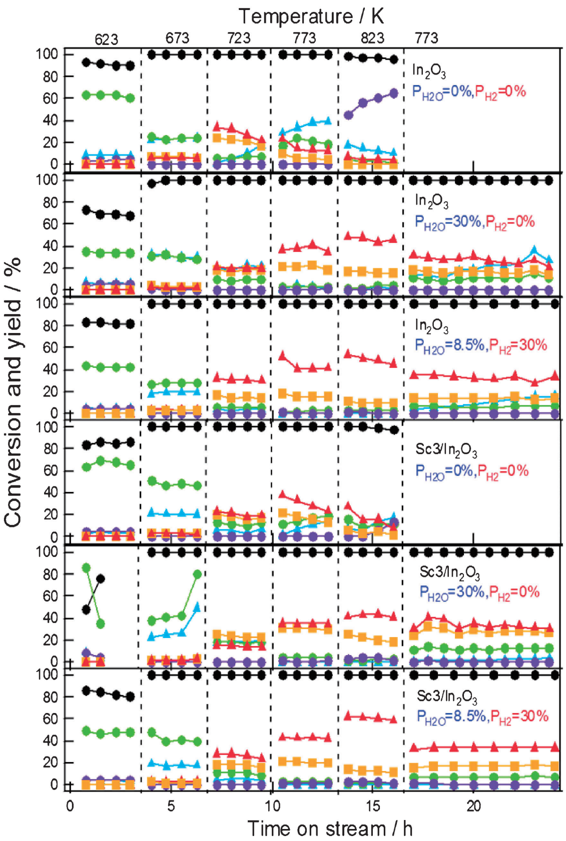

Figure 1. The catalytic activity of In_2O_3 and Sc(3)/In_2O_3 as a function of the reaction time and temperature. Reaction conditions: catalyst weight, 2.0 g; total flow rate, 12.8 mL min^{-1} (GHSV 687 h^{-1}); 1 atm; P_{EtOH}, 30 vol% (N_2 balance). Water and/or hydrogen were fed as necessary; P_{H_2O}, 8.5 vol%; P_{H_2}, 30 vol%. ● Conv. of EtOH, ▲ yield of propene, ▲ of acetone, ■ of iso-butene, ● of ethene, ● of acetaldehyde.

properties, ionic radii of metal ions, crystal structures of mixed oxides, and changes in the redox behaviors of In_2O_3 were all investigated as possible causes for the observed changes, but no satisfactory explanation could be obtained.

Among the first group of metals, the most effective additives for enhancement of propene formation were Sc and Ni. The change in catalytic activity with reaction time on Ni/In_2O_3, however, was large. In addition, as shown in Figure 2, the Ni/In_2O_3 was reduced and generated a mixed phase of In_2O_3, metallic In, and Ni_3In_2 alloy. In contrast, the Sc-loaded In_2O_3 was not reduced. The yields of propene (Table 1) and the anti-reducibility (Figure 2) indicated Sc/In_2O_3 as the most effective catalyst. The activity of Sc/In_2O_3 for the propene production decreased with the amount of Sc loaded, with the maximum activity being observed at 1–3 atom% Sc (Table 1). The results suggested that there would be a certain type of surface defects on In_2O_3 which might work as initiation sites of the reduction of oxide during the reaction and that the Sc atoms would be loaded on the sites to prevent the reduction. The situation and role of Sc added should be clarified in the near future.

The addition effect of water vapor was examined to avoid or reduce deactivation of the catalysts (Figure 1). The introduction of water could greatly improve the yield and stability of propene formation on the In_2O_3 and Sc/In_2O_3 catalyst. Within the present experiments, the addition of 10 vol% water led to significant improvement, but the effect was saturated above 10 vol% (results not shown). Next, hydrogen addition in the EtOH + H_2O + N_2 flow was examined because one could expect more efficient conversion of acetone to propene according to eq 3. As clearly shown in Figure 1, the hydrogen addition improved the

Table 1. Activity of various metal oxide-loaded In_2O_3 catalysts for the conversion of ethanol to lower olefins[a]

Additive (atom%)	React. Temp. /K	Yield calculated on carbon basis/%				
		C_3H_6	i-C_4H_8	C_2H_4	Acetone	AcH
None[b]	623	0.4	0.3	63.6	8.9	3.1
	673	6.3	7.3	25.1	22.5	0
	723	34.1	24.0	5.6	1.7	0
	773	23.5	10.5	16.5	28.8	0
	823	7.5	0	4.1	18.0	44.6
Li(10)	773	0.8	0.5	2.1	44.0	10.4
K(10)	773	7.6	5.1	12.9	40.6	0.0
Ca(10)	773	2.1	1.7	6.5	35.0	0.1
Ba(10)	773	3.2	1.7	8.7	36.5	2.3
Sc(1)	773	35.3	18.0	7.5	2.9	0.1
Sc(3)	773	34.0	19.1	10.8	3.7	0.2
Sc(3)[c]	773	42.9	20.6	2.8	0.2	1.1
	823	61.8	14.7	1.2	0.1	2.9
Sc(10)	773	33.8	19.5	8.7	0.7	0.0
Sc(20)	773	16.0	20.8	8.8	5.7	0.0
Y(10)	773	2.5	2.5	21.8	30.0	0.0
La(10)	773	2.4	1.8	18.5	31.7	0.0
Ce(10)	773	7.6	5.1	12.9	40.6	0.0
Er(10)	773	3.3	3.4	19.1	28.6	0.0
Ti(10)	773	7.9	6.0	3.1	33.1	0.1
Zr(10)	773	28.6	14.7	12.5	14.6	0.0
V(10)	773	26.3	20.4	6.4	5.4	0.2
Nb(10)	773	16.9	7.0	3.1	27.8	1.1
Cr(10)	773	28.0	13.6	9.3	10.7	0.1
Mo(10)	773	34.2	5.8	4.1	12.1	0.0
W(10)	773	2.6	2.3	6.4	0.1	34.6
Mn(10)	773	4.8	3.9	10.5	26.2	0.0
Fe(10)	773	5.2	4.1	14.0	37.9	0.1
Co(10)	773	27.6	14.3	7.3	15.5	0.0
Ni(10)	773	37.2	16.3	13.1	4.8	0.0
Pd(10)	773	16.8	9.9	10.9	16.0	0.0
Cu(10)	773	28.5	16.4	11.2	17.6	0.1
Zn(10)	773	18.3	11.0	7.6	24.5	0.0
Al(10)	773	8.4	7.0	8.4	30.3	0.1
Ga(10)	773	12.7	8.6	4.2	27.5	0.1
Sn(10)	773	4.1	4.5	3.6	33.3	4.0
Sb(10)	773	5.1	2.8	2.4	42.2	0.2
Bi(10)	773	3.2	3.2	4.2	23.4	33.3

[a] All of the results were obtained after 45 min. Reaction conditions were as follows unless otherwise stated: catalyst weight, 2.0 g; total flow rate, 12.8 mL min^{-1} (GHSV 687 h^{-1}); P_{EtOH}, 30 vol% (N_2 balance); 773 K; 1 atm. [b] Without any additive. [c] Water of 8.5% and hydrogen of 31.3% were added in the ethanol flow. The total flow rate and the partial pressure of ethanol were the same as those in the standard conditions.

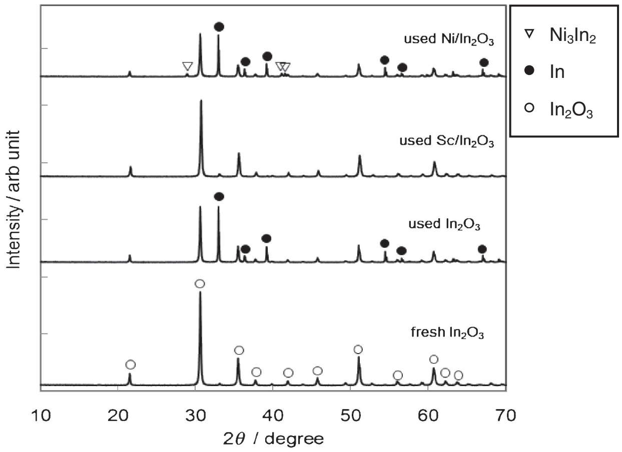

Figure 2. X-ray diffraction patterns of In_2O_3 (A) before reaction and In_2O_3 (B), Sc/In_2O_3 (C), and Ni/In_2O_3 (D) after reaction. Reaction conditions: catalyst weight, 2.0 g; total flow rate, 12.8 mL min^{-1} (GHSV 687 h^{-1}); P_{EtOH}, 30 vol % (N_2 balance); 1 atm.

yield of propene and the stability of the catalyst. The appropriate reaction conditions on Sc/In_2O_3 were found to be 8–10% water and 30–50% hydrogen with 30% EtOH.

This reaction system gave the best conversion for propene and long-term stability. Specifically, the catalytic activity of Sc/In_2O_3 was greatly stabilized with little decrease after 50 h of continuous service. It should be noted in Figure 1 that the product distributions on In_2O_3 in the presence of water and hydrogen were similar to those on Sc/In_2O_3 but the increase in acetone formation on the former around 20 h would indicate the low stability of In_2O_3 without the Sc addition. As shown in Table 1, the propene yield reached 61.8% at 823 K on Sc(3)/In_2O_3. The yield corresponded to 82% of the theoretical conversion level (75%) based on Reaction 4. Such high and stable yield of propene has not been reported for zeolites or other catalysts.

The molar ratio of propene and acetone, A_{C3}, with that of carbon dioxide, A_{CO_2}, was first verified to be 3:1 based on Reactions 2 and 4. In the calculation, the A_{CO_2} values were replaced with the total amounts of carbon dioxide and carbon monoxide, A_{CO_x}, because the progress of Reaction 5 was confirmed on the catalyst. In addition, as isobutene formation was revealed to go through acetone as an intermediate (results in separated pulse experiments, not shown), the formation reaction was assumed to be Reaction 6 and the A_{C3} values were corrected for quantities of isobutene, A_{C4}. Namely it was verified whether eq 7 was to be followed or not in the product distributions. The yields of propene, acetone, isobutene, CO_2, and CO on Sc(3)/In_2O_3 at 773 or 823 K in Table 1 were 42.9, 0.2, 20.6, 11, and 12, or 61.8, 0.1, 14.7, 10, and 17, respectively. Using these values, the left-hand side of eq 7 was 24.7 or 28.0, and the right-hand side was 23 or 28. The excellent consistency strongly indicated that the total reactions shown in Reactions 4 and 6 were correct.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (5)$$

$$3CH_3CH_2OH + H_2O \rightarrow CH_2{=}C(CH_3)_2 + 2CO_2 + 6H_2 \qquad (6)$$

$$A_{C3}/3 + A_{C4}/2 = A_{CO_x} \qquad (7)$$

The rough reaction path EtOH → acetaldehyde → acetone → propene was suggested in Reactions 1–3. The conversion of EtOH to acetaldehyde and of acetone to propene in H_2 were widely reported to proceed on various catalysts and identified on the In_2O_3 catalysts. However, the reaction to form acetone from acetaldehyde, Reaction 2, remained unclear.[14–21]

A novel and complicated reaction route from ethanol to propene was found on Sc-modified In_2O_3 catalysts. The yield of propene reached approximately 60% based on the carbon balance. The addition of Sc prevented the reduction of In_2O_3 catalysts, while water vapor decreased coke formation. Both additives increased the lifetime of the catalysts. In addition, cofeed of hydrogen increased the yield of propene because of the selective hydrogenation–dehydration of intermediate acetone. The findings shed light on the novel, one-step, and sustainable production of propene from renewable bio-ethanol instead of the present thermal or catalytic cracking of naphtha.[22,23]

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