



Selective catalytic conversion of bio-ethanol to propene: A review of catalysts and reaction pathways



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ABSTRACT

The conversion of ethanol to propene were examined on Ni ion-loaded silica MCM-41(Ni-M41), Sc-modified In_2O_3 (Sc/ In_2O_3), and a solid solution of Y_2O_3 - CeO_2 . The propene production activity was in the order, Sc/ In_2O_3 > Y_2O_3 - CeO_2 > Ni-M41, while their stability during the reaction was Y_2O_3 - CeO_2 ~ Sc/ In_2O_3 > Ni-M41. The propene yield and durability of Sc/ In_2O_3 were greatly improved by addition of water and hydrogen in the reactant stream. The reaction mechanism was greatly dependent on the catalyst employed. On Ni-M41, the metathesis reaction of ethene and butenes, produced through dimerization of ethene, was a key step for the propene formation. On the remaining two oxide catalysts, the major pathways were the common: ethanol \rightarrow acetaldehyde \rightarrow acetone \rightarrow propene. The detailed reaction pathways, however, were different from each other. On Sc/ In_2O_3 , acetaldehyde was oxidized to acetic acid with water or a surface hydroxyl group and the resulting acetic acid was converted to acetone and carbon dioxide through ketonization. On the other hand, on Y_2O_3 - CeO_2 , acetaldehyde was converted to ethyl acetate, and then it decomposed to form acetic acid and ethene. Acetic acid was converted to acetone and carbon dioxide in the same manner as that on Sc/ In_2O_3 . The by-production of much amounts of ethene was characteristic on Y_2O_3 - CeO_2 . On the Sc/ In_2O_3 oxide, a hydrogen molecule was active for the hydrogenation of acetone to 2-propanol. In contrast, on the Y_2O_3 - CeO_2 oxide, hydrogenation of acetone did not proceed with hydrogen but did with the co-fed ethanol, that is, by the Meerwein-Ponndorf-Verley reduction.

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1. Introduction

The use of bioethanol (bEtOH) as an alternative (or additive) for automobile fuels has increased rapidly all over the world. This is one way of using renewable resources to suppress carbon dioxide emissions, while another challenge is the conversion of bEtOH to various olefins and their use for production of chemicals and polymers [1–7]. The latter would be very significant for the long-term fixation of carbon dioxide. Many efforts have therefore been devoted to the development of systems for converting bEtOH to ethene and other lower olefins. In particular conversion to propene is desirable due to the greater demand for propene derivatives, such as propene oxide, acrylonitrile, and polypropene [2].

Catalytic conversions of EtOH on zeolites [3–5] and metal oxides [6,7] have widely been studied. On zeolites, the activity and selectivity in the many studies reported so far are insufficient. The major weakness is catalyst deactivation. For example, the

selectivity towards propene on proton- or metal-modified zeolites is usually ca. 20–30% and decreases with reaction time, although sometimes higher propene selectivity values are observed upon catalyst degradation [3–5]. Oligomerization, polymerization, and fission reactions on strong acid sites in zeolite pores result in the formation of propene and butenes due to shape selectivity [3–5]. However, the random reactions in the pores finally result in coke formation and short catalyst life times. EtOH can also react on metal oxide surfaces to give various chemicals. Acid sites are widely recognized to lead to dehydration of EtOH, giving ethene, while basic sites lead to dehydrogenation to yield acetaldehyde [6,7]. As a result, many kinds of products, for example aldehydes, ketones, ethene, and butenes, have been observed on oxide catalysts. In this catalysis, butenes and other higher olefins are produced by oligomerization of ethene, but as far as we are aware significant propene production on oxide catalysts has not been reported.

At first, our attention was devoted to nickel ion-loaded mesoporous silica MCM-41 (Ni-M41) because it was active towards the synthesis of propene from ethene, by dimerization of ethene and subsequent metathesis of the resulting butenes with unreacted ethene [8]. Therefore, Ni-M41 is a possible catalyst for the

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conversion of EtOH to propene since M41 is active for the dehydration of EtOH to yield ethene [8b]. Indeed, this was confirmed by our group [9] and subsequently by Sugiyama et al. [10]. The pore diameters of M41 are usually 1.5–5.0 nm, and, therefore the product distribution on the catalysts is not controlled by shape selectivity. The reaction pathways are of interest.

On the other hand, 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 [11,12]. Our attention was paid to the selective conversion of C_x -alcohol to C_{2x-1} -ketone on ceria-based catalysts [11], 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 CeO_2 (Y_2O_3 - CeO_2) was found by us to show the stable catalytic activity for the selective conversion of ethanol to propene [13]. We also found that not only Y_2O_3 - CeO_2 but also Sc-modified In_2O_3 (Sc/In_2O_3) [14] offered new types of catalysis for the production of propene without shape selectivity, though the catalytic activity of In_2O_3 gradually decreased with duration at 30 vol% of ethanol.

In this review article, we first summarized the catalytic activity of the above three catalysts, Ni-M41, Y_2O_3 - CeO_2 , and Sc/In_2O_3 . The effects of the additives for the In_2O_3 catalysts were also discussed. Then, it will be shown that the reaction pathways are greatly dependent on the catalysts employed, in which ethene and acetaldehyde worked as respective intermediates on Ni-M41 and on the oxide catalysts.

2. Catalytic activity of Ni-M41, Sc/In_2O_3 , and Y_2O_3 - CeO_2

The catalytic activity of these three oxides was studied as a function of the partial pressures of ethanol, water, and hydrogen, the reaction temperature, the reaction time, and the space velocity. The effects of kinds and amounts of metal ions added on the respective catalysts were also investigated. When we examined the catalytic activity, deactivation of the catalysts was observed, which was enhanced under the high partial pressure of ethanol. For example, the propene yield on Ni-M41 was approximately 17% at $P_{ethanol} = 5.5\%$ and did not change in 10-h experiment [15], while at $P_{ethanol} = 30\%$ the conversion degree to propene was 23% at the initial stage and decreased to 12% after 10 h. Since the high concentration of ethanol is essential to reduce running costs of the industrial processes, the experimental results indicated difficult employment of Ni-M41 in the practical process.

Typical experimental results on these catalysts are summarized in Table 1. The experimental conditions were adjusted to respective appropriate ones at which the propene yields were maximized. For example, addition of hydrogen gas into the reactants' gas flow was very effective for the Sc/In_2O_3 catalyst but showed no effect for the Y_2O_3 - CeO_2 catalyst. This is due to the difference of hydrogenation mechanisms of intermediate acetone on these two catalysts, as will be shown in the sections of reaction pathways. The activity order of these three catalysts for the production of propene was $Sc/In_2O_3 \gg Y_2O_3$ - $CeO_2 > Ni$ -M41. The yield of propene on the Sc/In_2O_3 catalyst reached at 60–65% which was approximately 80% of the theoretical maximum, 75% (as shown later), and sufficiently high in the heterogeneous catalysis. Such high and stable yield of propene has never been reported for zeolites or other catalysts for the conversion of ethanol. The major by-products were iso-butene and carbon dioxide on Sc/In_2O_3 , while ethene on the remaining two catalysts. The great distinction among the product distributions clearly resulted from the difference of reaction pathways.

The effects of scandium addition onto the In_2O_3 catalyst and of the reaction conditions were introduced here in more detail. The

disadvantages of not-modified In_2O_3 were deactivation mainly due to the reduction of In_2O_3 to In metal and carbon deposition, and low selectivity of propene due to the by-production of acetone. The addition of only 1–3 at% of Sc onto In_2O_3 improved the anti-reducibility of In_2O_3 . We 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 similarity of the radius of Sc^{3+} ion of six-coordination, 0.75 nm, to that of six-coordinated In^{3+} ion, 0.80 nm, might support the suggestion. 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 owing to the carbon deposition. The amounts of carbon deposits determined by TG-DTA analysis after the use in reaction decreased to about 1/10–1/20 by the water addition. The introduction of water could also improve the yield and stability of propene formation on the Sc/In_2O_3 catalyst. Next, hydrogen addition in the $EtOH + H_2O + N_2$ flow was examined because one could expect more efficient conversion of acetone to propene. Clearly, the hydrogen addition improved the yield of propene and the stability of the catalyst. In addition, the amount of carbon deposit greatly decreased upon the co-feed of water and hydrogen with EtOH. The appropriate reaction conditions on Sc/In_2O_3 were found to be 8–25% water and ca. 30% hydrogen with 30% EtOH.

In contrast to Sc/In_2O_3 , the active phase of Y_2O_3 - CeO_2 was the surface solid solution. Upon applying the conventional impregnation method for Y_2O_3 on CeO_2 , the catalytic activity showed the volcano-shaped dependence on the amount of added Y. The appropriate loading amount of Y was approximately 20 at%, at which a 1:1 solid solution was produced on the surface. Based on the EXAFS, FT-IR, and TPD results, it was indicated that the densities of oxygen vacancies on the catalysts did not change with the loading of Y_2O_3 but the numbers of strong acid sites decreased at the 20 at% Y loading. The maximized catalytic activity would be due to the decreasing ethene yield resulting from the elimination of active acid sites.

The surface structure of Ni-M41 is complicated and still has exactly been undetermined. Various physicochemical techniques were employed to characterize the coordination numbers of oxygen and silicon around a nickel ion loaded on the pore wall of mesoporous silica, their changes with the pore structure and the Si/Ni ratio, and the dependence of the redox behavior of nickel ions on the preparation methods. The findings indicated the formation of a three coordinated Ni^{2+} ion located on five membered Si-O rings. Besides this species, a four coordinated Ni^{2+} species was found to be formed on six membered Si-O rings. Both species constructed a 2:1 nickel phyllosilicate-like structure after the calcination. The three coordinated species was suggested as an active species for the present reaction and its amount was dependent on the pore diameter and the Si/Ni ratio.

The reaction mechanisms including for example the surface structures, the adsorption sites, and the states of intermediates have not been resolved yet, and the relation between the structure of catalyst and the reaction pathway has not been clarified. However, the reaction pathways on the respective catalysts were essentially elucidated and will be introduced in the next sections.

3. Reaction pathways on Ni-MCM-41

The product distribution was studied as a function of space velocity on Ni-M41 at 673 K. The dependence is summarized in Fig. 1. At $SV = 70,000 h^{-1}$ the conversion level of EtOH was ca. 50%, but at 20,000 or below it increased to 95% or more. The product

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