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Dehydration of 5-amino-1-pentanol over rare earth oxides

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ABSTRACT

Vapor-phase catalytic dehydration of 5-amino-1-pentanol was investigated over various oxide catalysts including rare earth oxides (REOs). Over ordinary acidic oxides such as Al_2O_3, SiO_2, SiO_2-Al_2O_3, TiO_2, and ZrO_2, a cyclic amine such as piperidine was mainly produced at temperatures of 300 °C and higher. In contrast, basic REOs with a cubic bixbyite structure showed the catalytic activity in the conversion of 5-amino-1-pentanol to produce 4-penten-1-amine at 425 °C. In REO catalysts, Tm_2O_3, Yb_2O_3, and Lu_2O_3 showed the high conversion of 5-amino-1-pentanol and the high selectivity to 4-penten-1-amine. Especially, Yb_2O_3 calcined at 800 °C showed a high formation rate of 4-penten-1-amine with the selectivity of ca. 90% at 425 °C. In comparing the reactivity of several amino alcohols to form the corresponding unsaturated amines, Yb_2O_3 effectively catalyzed the dehydration of 6-amino-1-hexanol into 5-hexen-1-amine, whereas 3-amino-1-propanol and 4-amino-1-butanol were not effectively dehydrated due to the decomposition of the reactant.

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1. Introduction

Unsaturated amines, which have both a carbon double bond and an amino group in the molecule, can be used for various applications such as polymer, ion-exchange membrane, raw material of chemical, pharmaceutical and agricultural chemical intermediates. As a pioneering report, Zimmermann et al. have reported that unsaturated amines can be produced by hydroaminomethylation of olefins using three gases such as H_2, CO, and NH_3 [1]. In the method, however, the resulting primary amines are further converted into the secondary amine. Nicolai et al. have showed that 4-penten-1-amine is produced by reduction of 4-pentenamido [2], while 4-penten-1-amine is produced with a low yield, which is approximately 40%.

We have previously reported a novel catalytic synthesis process of unsaturated alcohols via the dehydration of alkanediols such as 1,5-pentanediol [3–5], 1,4-butanediol [5–8], and 1,3-butanediol [5,9–11] over rare earth oxides (REOs) calcined at 800 °C. In the dehydration of 1,5-pentanediol, heavy REOs such as Lu_2O_3, Yb_2O_3, and Tm_2O_3 are highly active and selective for the formation of 4-penten-1-ol, and the highest selectivity of 4-penten-1-ol was 80.3% over Tm_2O_3 calcined at 800 °C [4,5]. It is also known that REOs [12,13] as well as ZrO_2 [14–16] and CeO_2-ZrO_2 [17] have unique character to catalyze the dehydration of 2-alcohol to produce α-olefin via Hoffman elimination. We have also reported the dehydration of 1,4-butanediol as well as 1,5-pentanediol over composite oxides of cubic $Sc_{2-x}Yb_xO_3$ (x = 0.5, 1.0, and 1.5) [18]: the highest selectivity to 3-buten-1-ol surpassed 80% in the dehydration of 1,4-butanediol over the $Sc_{2-x}Yb_xO_3$ (x = 0.5, 1.0, and 1.5) catalysts calcined at 800 °C. Thus, we expected that REOs could work effectively in the dehydration of amino alcohols.

In this work, we investigated the dehydration of 5-amino-1-pentanol into 4-penten-1-amine over REOs and $Sc_{2-x}Yb_xO_3$ (x = 0.5, 1.0, and 1.5) at 425 °C to search a suitable catalyst and the efficient reaction conditions. We have found that 4-penten-1-amine is efficiently produced over Tm_2O_3, Yb_2O_3, and Lu_2O_3 in the dehydration of 5-amino-1-pentanol (Scheme 1). We also investigated the catalytic features of Yb_2O_3 in the dehydration of 5-amino-1-pentanol. Furthermore, we performed other amino alcohols with different carbon chain length, such as 3-amino-1-propanol, 4-amino-1-butanol, and 6-amino-1-hexanol, to produce the corresponding unsaturated amines over Yb_2O_3.

2. Experimental

2.1. Catalyst samples

Metal nitrate hydrates, such as $Ce(NO_3)_3$, $Nd(NO_3)_3$, $Sm(NO_3)_3$, $Eu(NO_3)_3$, $Gd(NO_3)_3$, $Tb(NO_3)_3$, $Ho(NO_3)_3$, $Y(NO_3)_3$, $Er(NO_3)_3$,

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Scheme 1. Dehydration of 5-amino-1-pentanol to 4-penten-1-amine.

$Tm(NO_3)_3$, $Yb(NO_3)_3$, $Lu(NO_3)_3$, and $Sc(NO_3)_3$, were purchased from Sigma-Aldrich Co., Ltd., Japan. La_2O_3, Pr_6O_{11}, $Mg(NO_3)_2$, $Ca(NO_3)_2$, and $Dy(NO_3)_3$ hexahydrate were purchased from Wako Pure Chemicals Co., Japan. 5-Amino-1-pentanol, 3-amino-1-propanol, and 4-amino-1-butanol were purchased from Wako Pure Chemicals Co., Japan. 6-Amino-1-hexanol aqueous solution (70 wt.%) was purchased from Sigma-Aldrich Co., Ltd., Japan.

Except La_2O_3 and Pr_6O_{11}, other REOs such as CeO_2, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, and Sc_2O_3 were prepared by the calcination of the corresponding nitrate. MgO and CaO were also prepared by the calcination of the corresponding nitrate. Monoclinic Yb_2O_3 was supplied by Kanto Kagaku Co., Ltd., Japan. Three $Sc_{2-x}Yb_xO_3$ ($x = 0.5$, 1.0, and 1.5) catalysts were supplied by Daiichi Kigenso Kagaku Kogyo Co., Ltd., Japan [18]. Rutile TiO_2 (JRC-TIO-3) and anatase TiO_2 (JRC-TIO-4) were supplied by Catalyst Reference of Japan. Amorphous SiO_2 (CARiACT Q10) was supplied by Fuji Silycia Chemical Ltd. Monoclinic ZrO_2 (RSC HP) and tetragonal ZrO_2 were supplied by Daiichi Kigenso Kagaku Kogyo Co., Ltd., Japan and Saint-Gobain, respectively. Al_2O_3 (N611N) and SiO_2-Al_2O_3 (N631L) were purchased from Nikki Chemical Co., Ltd., Japan.

2.2. Catalytic reaction

The dehydration of amino alcohols, such as 5-amino-1-pentanol, 3-amino-1-propanol, 4-amino-1-butanol, and 6-amino-1-hexanol, were carried out in a fixed-bed down flow reactor with an inside diameter of 20 mm under the atmospheric pressure of either N_2 or H_2 gas. In each test, 0.5 g of catalyst was loaded into the reactor. Amino alcohols were dehydrated at temperatures between 300 and 450 °C. Prior to the reaction, the catalyst was preheated in the flow reactor in a carrier gas at the same temperature as the reaction temperature for 1 h. After the pretreatment, an amino alcohol was fed through the top of the reactor at a liquid feed rate of 1.71 $cm^3\ h^{-1}$, which corresponds to 16 $mmol\ h^{-1}$ for 5-amino-1-pentanol and $W/F = 31\ g_{cat.}\ h\ mol^{-1}$ where W is catalyst weight and F is a reactant feed rate, together with a carrier gas flow of 20 $cm^3\ min^{-1}$. An effluent mixture collected every hour was analyzed by gas chromatography (GC-8A, Shimadzu, Japan) with a capillary column of TC-5 (30m, GL Science Inc., Japan) over a temperature range controlled from 70 to 280 °C at a heating rate of 10 °C min^{-1}. The major products in the dehydration were 4-penten-1-amine, piperidine, tetrahydropyridine, δ-valerolactam, and *n*-pentyl amine.

Since the catalytic activity is stable in the similar manner to the previous works reported in the dehydration of diols [3–11], the conversion of 5-amino-1-pentanol and the selectivity to each product were averaged in the 1–5 h to evaluate the catalytic activity. The formation rate of the corresponding unsaturated amines per unit surface area [$mmol\ h^{-1}\ m^{-2}$] was calculated by using the feed rate of the reactant multiplied by the conversion and the selectivity divided by the catalyst weight and specific surface area.

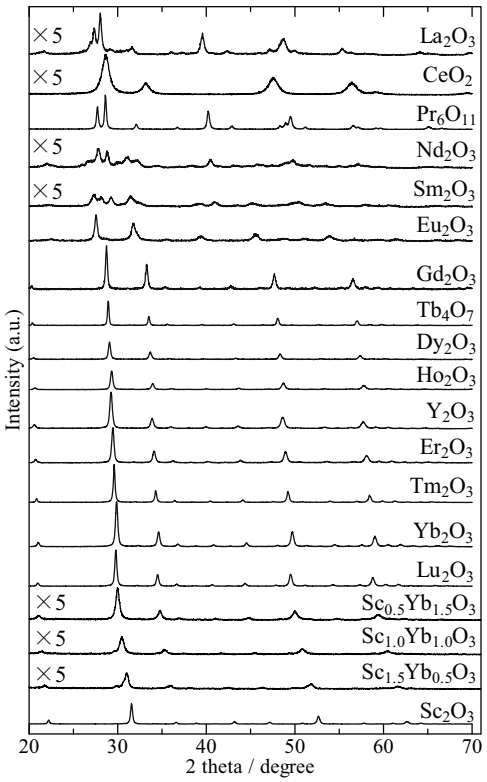

Fig. 1. XRD profiles of REO and $Sc_{2-x}Yb_xO_3$ samples calcined at 800 °C.

2.3. Characterization

The specific surface area (SA) of each catalyst was calculated by the BET method using the N_2 isotherm at −196 °C. X-ray diffraction (XRD) patterns were recorded on an XRD7000 (Shimadzu, Japan) using Cu Ka radiation (λ = 0.15 nm) to detect the crystal structure of the samples. The tube voltage and current were 40 kV and 40 mA, respectively.

Temperature-programmed desorption (TPD) of adsorbed CO_2 was measured to estimate the basicity of the catalysts. The numbers of basic sites were estimated from neutralization–titration curves of diluted NaOH solution [19,20]. Prior to the CO_2 adsorption, a sample (ca. 50 mg) was preheated in a quartz tube at 500 °C for 1 h under a reduced pressure. In CO_2-TPD, CO_2 was adsorbed on the sample at room temperature for 72 h and evacuated for 1 h. After no CO_2 had been observed in N_2 flow at room temperature, the sample was heated from room temperature to 800 °C at a heating rate of 10 °C min^{-1} in an N_2 flow of 34 $cm^3\ min^{-1}$. The desorbed CO_2 molecules, together with N_2 gas, were bubbled into an electric conductivity cell containing a dilute NaOH solution (50 cm^3). The conductivity of the solution was monitored, and the resulting conductivity curve was differentiated to provide a distribution curve of CO_2 desorbed from adsorbent.

3. Results

3.1. Characterization of REOs

Fig. 1 shows the XRD patterns of REOs and $Sc_{2-x}Yb_xO_3$ calcined at 800 °C. REO samples had different crystal structures with A-, B-, C-, and C_F-type [21,22]. Light REOs such as La_2O_3, Pr_6O_{11}, and Nd_2O_3 had a hexagonal structure of A-type. Other light REOs such as Sm_2O_3 had a monoclinic structure of B-type. On the other hand, heavy REOs such as Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, Sc_2O_3, and $Sc_{2-x}Yb_xO_3$ ($x = 0.5$, 1.0, and 1.5) [18] had a cubic bixbyite structure of C-type. Eu_2O_3 had an unknown phase, and CeO_2 had a cubic fluorite structure of C_F-type. The crystal phases of REOs and $Sc_{2-x}Yb_xO_3$ as well as their SA are summarized in Table 1.

Fig. 2 shows TPD profiles of CO_2 adsorbed on the REOs. Several desorption peaks of CO_2 from light REOs, such as La_2O_3, CeO_2,

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