

Catalytic reaction of 1,3-butanediol over rare earth oxides

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Abstract

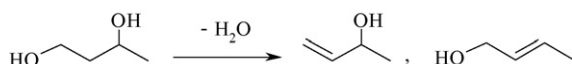
Vapor-phase reaction of 1,3-butanediol was investigated over rare earth oxide (REO) catalysts. In the reaction of 1,3-butanediol, dehydration and decomposition of 1,3-butanediol occurred simultaneously at 325 °C. The formation of unsaturated alcohols such as 3-buten-2-ol and *trans*-2-buten-1-ol was predominant over CeO₂, Sc₂O₃, and Tm₂O₃, while 1,3-butanediol was preferentially decomposed over the other REOs. Especially, light REOs such as La₂O₃, Pr₆O₁₁, Nd₂O₃, and Sm₂O₃, catalyzed decomposition of 1,3-butanediol into 2-propanol, propanone, methanol, and ethanol. Basic and acidic properties of REOs were measured with temperature-programmed desorption (TPD) of adsorbed CO₂ and NH₃, respectively. The surface character of REOs was basic but not acidic. Both strength and number of basic sites of REOs increased with increasing ionic radius of rare earth cation in the REO except CeO₂: light REOs were more basic. The decomposition of 1,3-butanediol would be attributed to the basicity of catalyst. In the reaction of 1,3-butanediol as well as 1,4-butanediol, the catalytic function of REOs will be discussed in connection with lanthanide contraction.

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1. Introduction

Cerium (IV) oxide, CeO₂, is an attractive catalyst for converting chemicals into valuable compounds. In the dehydration of 1,3-diols, unsaturated alcohols are selectively formed over pure CeO₂ [1–4]: 3-buten-2-ol and *trans*-2-buten-1-ol are produced from 1,3-butanediol at 325 °C with the selectivity of 58 and 37 mol%, respectively. In contrast, solid acids such as silica–alumina, alumina, and titania catalyze non-selective dehydration of 1,3-butanediol into several unsaturated alcohols as well as various types of reactions such as isomerization and further dehydration of the product unsaturated alcohols [5].



Pure CeO₂ is the only catalyst that can catalyze the selective dehydration of 1,3-diols to the corresponding unsaturated

alcohols among various oxide catalysts [1,5]. We speculated the reaction mechanism in the dehydration of 1,3-diols into unsaturated alcohols over CeO₂ (Fig. 5 in Ref. [2]). Initially, a H atom at 2-position and two OH groups of 1,3-diol coordinate to three Ce cations exposed on an oxygen-defect site. Then, the 2-position H atom is withdrawn by a Ce⁴⁺ cation, and finally, an OH group is radically extracted to yield unsaturated alcohols, and the OH radical and the hydrogen atom recombined to be H₂O. We have executed quantum calculations for the adsorption of 1,3-butanediol on an oxygen-defect site of CeO₂(1 1 1) surface [6,7]. The active site for the selective dehydration of 1,3-diols is proved to be an oxygen-defect site of CeO₂(1 1 1) surface.

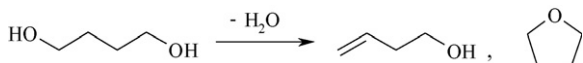
CeO₂ also catalyzes the formation of 3-buten-1-ol in the dehydration of 1,4-butanediol [3,8]: 3-buten-1-ol is produced with maximum selectivity of 68 mol% over CeO₂ at 400 °C, whereas several side reactions such as isomerization, dehydrogenation, hydrogenation of 3-buten-1-ol as well as further dehydration into 1,3-butadiene proceed, together with the cyclization of 1,4-butanediol into tetrahydrofuran (THF) and γ -butyrolactone. We have found that 1,4-butanediol is dehydrated to produce 3-buten-1-ol over monoclinic ZrO₂ [9,10]. The selectivity to 3-buten-1-ol surpasses 70 mol% over Na-modified ZrO₂ at 325 °C. The addition of Na onto ZrO₂

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effectively suppresses side reactions such as cyclization into THF. In the latest paper, we have reported that several rare earth oxide (REO) catalysts such as Tb_4O_7 , Er_2O_3 , and Yb_2O_3 are selective for the production of 3-buten-1-ol from 1,4-butanediol [11]: the selectivity to 3-buten-1-ol exceeds 80 mol% over Yb_2O_3 .



ZrO_2 and REOs are known to have attractive catalytic features, i.e. Hoffmann elimination ability in the dehydration of 2-alcohols such as 2-butanol and 2-octanol [12–15]: α -olefin such as 1-butene is formed with the selectivity higher than 80% in the dehydration of 2-butanol over REOs, except for La_2O_3 and CeO_2 [13]. In the dehydration of 2-octanol over REOs, dehydrogenation to 2-octanone simultaneously proceeds with the formation of 1-octene [14]. The redox cycle of Ce^{4+} – Ce^{3+} plays an important role in the dehydration in the dehydration of diols [3]. In contrast, acid–base property of ZrO_2 plays a role for the dehydration of 1,4-butanediol [10]. Except for CeO_2 , REOs usually have stable 3+ cations, and the dehydration of diols could be affected by acid–base property of REOs, which is not clarified.

In this paper, we measured acid–base property of REOs and examined dehydration of 1,3-butanediols over REOs. We described the characteristic catalytic property correlated with the surface basic property of REOs, connecting with lanthanide contraction. We also discussed the catalytic activity of REOs in the dehydration of 1,4-butanediol concerning with the basic property.

2. Experimental

2.1. Samples

1,3-Butanediol was purchased from Wako Pure Chemical Industries, Japan. It was used for the catalytic reaction without further purification. CeO_2 and ZrO_2 were supplied by Daiichi Kigenso Co. Ltd., Japan. The other REO samples were purchased from Kanto Kagaku Co. Ltd., Japan. It has been announced that the commercial REO samples are prepared in the decomposition of the corresponding chlorides at temperatures >2000 °C for ca. 2 s in a vapor phase. Table 1 enumerates the samples used in this study.

2.2. Characterization

Specific surface area (SA) of 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 $\text{Cu K}\alpha$ radiation ($\lambda = 0.15$ nm) to detect the crystal structure of the samples. The tube voltage and current were 40 kV and 30 mA, respectively.

The temperature-programmed desorption (TPD) of adsorbed CO_2 was examined by neutralization titration using an electric conductivity cell immersed in an aqueous solution, as has been described elsewhere [10,16]. A sample (ca. 30 mg)

Table 1
Properties of REOs used in the reactions

Catalyst	SA ^a ($\text{m}^2 \text{g}^{-1}$)	IR ^b (nm)	Crystal phase ^c	Basic sites ($\mu\text{mol g}^{-1}$)	Acidic sites ($\mu\text{mol g}^{-1}$)
Sc_2O_3	98.4	0.0870	C	191	–
Y_2O_3	39.4	0.1019	M	674	–
ZrO_2	99.7	0.084 ^d	M	232 ^e	82.1 ^e
La_2O_3	55.3	0.1160	H	2000	0
CeO_2^f	23.0 ^f	0.097 ^d	C	81.6	–
Pr_6O_{11}	55.2	0.1126	H	1280	0
Nd_2O_3	55.2	0.1109	H	1460	0
Sm_2O_3	49.3	0.1079	M	1180	–
Eu_2O_3	62.9	0.1066	M	514	–
Gd_2O_3	46.7	0.1053	M	658	–
Tb_4O_7	38.7	0.1040	H + C	569	0
Dy_2O_3	44.2	0.1027	M	228	–
Ho_2O_3	43.7	0.1015	M	835	–
Er_2O_3	39.0	0.1004	M	424	0
Tm_2O_3	50.2	0.0994	M	718	–
Yb_2O_3	55.9	0.0985	M	600	0
Lu_2O_3	56.8	0.0977	M	202	–

^a SA: specific surface area.

^b IR: ionic radius for the trivalent ions with 8 coordination number; data cited from Ref. [30].

^c M, monoclinic; H, hexagonal; C, cubic.

^d IR values for the Zr^{4+} and Ce^{4+} ions with 8 coordination number; data cited from Ref. [30].

^e Basicity and acidity data cited from Table 2 of Ref. [10].

^f The sample was calcined at 900 °C. Reaction data cited from Table 1 of Ref. [4].

was preheated in a quartz tube at 500 °C for 1 h under a reduced pressure of 1.3 Pa. After the pretreatment, the quartz tube was filled with CO_2 gas at room temperature and ambient pressure for 72 h. The desorbed CO_2 , together with N_2 gas, was bubbled into a NaOH solution (50 cm^3) with the concentration of 1.0 mmol dm^{-3} . After no CO_2 had been observed in the N_2 flow, the sample was heated from 25 to 800 °C at a heating rate of 10 °C min^{-1} under N_2 flow of $15 \text{ cm}^3 \text{ min}^{-1}$. The amount of desorbed CO_2 was monitored by the change in the conductivity of the solution. A cumulative amount of desorbed CO_2 was obtained as a function of the desorbed temperature and then differentiated to give a TPD profile as a base strength distribution. The number of the basic sites is defined as the number of desorbed CO_2 in the temperature range from 25 to 800 °C by an assumption in which one CO_2 molecule adsorbs on a basic site of the catalyst surface.

The TPD of adsorbed NH_3 was measured by neutralization titration in the same way as the CO_2 TPD mentioned above, as has been described previously [10,16–19]. A sample (ca. 50 mg) loaded in a quartz tube was heated at 500 °C for 1 h under a reduced pressure of 1.3 Pa. NH_3 vapor with 13 kPa was introduced to the sample at 25 °C for 1 h, and then evacuated at 25 °C for 1 h to remove the NH_3 physisorbed on the catalyst. After no NH_3 had been observed in N_2 flow, the sample was heated from 25 to 800 °C at a heating rate of 10 °C min^{-1} . N_2 gas with the desorbed NH_3 was bubbled into H_2SO_4 solution with the concentration of 0.5 mmol dm^{-3} . In this paper, the number of the acidic sites is calculated in the temperature range from 25 to 800 °C.

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