



Selective conversion of ethanol to 1,3-butadiene using germanium talc as catalyst



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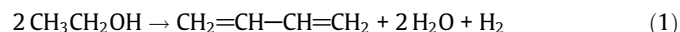
ABSTRACT

Preparation conditions of the germanium talc catalyst, which selectively produces 1,3-butadiene in the conversion of ethanol, were investigated. Furthermore, the influence of the reaction variables on the rate and selectivity of 1,3-butadiene formation was examined at 673 K. The electronic properties of the germanium talc were elucidated by O_{1s}, Mg_{2p}, and Ge_{3d} X-ray photoelectron measurements, while the atomic charges of these atoms were estimated by DFT calculations. Subsequently, the role of the oxygen atoms on the surface of the germanium talc to produce 1,3-butadiene was discussed on the basis of the afforded results.

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1. Introduction

Currently, 1,3-butadiene (butadiene henceforth) is predominantly produced *via* extractive distillation of a C4 fraction (hydrocarbons with four carbon atoms) from naphtha steam crackers used for the production of ethylene. Butadiene has also been synthesized by the conversion of ethanol. This reaction was discovered by Lebedev a century ago [1], and is expressed by the following overall stoichiometric reaction (Eq. (1)):



Eq. (1) represents a series successive reaction that can be separated into four key steps, as shown in Scheme 1 [2,3].

Step I is the oxidation of ethanol to acetaldehyde (CH₃CHO). Step II is the self-aldol condensation of acetaldehyde into crotonaldehyde via the dehydration of 3-hydroxybutanal. Step III is the reduction of crotonaldehyde to crotyl alcohol, while the final step, Step IV, is the dehydration of crotyl alcohol into butadiene. Step I is often referred to as the “dehydrogenation of ethanol” into acetaldehyde, while Step III is often referred to as the “Meerwein-Ponndorf-Verley-Oppenauer reduction” (MPVO reduction) of crotonaldehyde with ethanol.

The multistep nature of this transformation may be related to the use of multi-component catalysts, such as MgO–SiO₂, in order

to ensure excellent catalytic activities. For that reason, different binary, and ternary metal oxides (for example MgO–SiO₂) have been usually studied as catalysts for this reaction [3–10]. Among these catalysts, MgO was often contained as a major component, and the proposed mechanisms were usually based on the bifunctional properties of the mixed metal oxide catalysts [11,12].

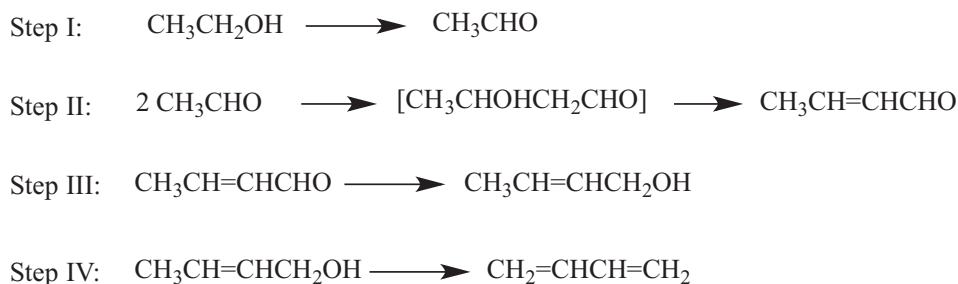
Chieragato et al. showed that all the most relevant steps of butadiene formation from ethanol are explained based on the surface properties of MgO alone, and that the acidic properties of silica are only needed to facilitate the final step of crotyl alcohol dehydration [13]. However, their MgO catalyst, which was prepared by the calcination of Mg(OH)₂, showed much lower selectivity than those observed with various mixed oxides, such as MgO–SiO₂.

We also have reported that MgO alone catalyzes the reaction expressed by Eq. (1) [14]. In this study, MgO catalyst was prepared by combining calcination and hydrothermal heating. The MgO catalyst showed almost the same selectivity (~50%) as various mixed oxides, such as MgO–SiO₂ [14]. This observation led us to reconsider the catalysis process for the conversion of ethanol into butadiene from the perspective of the characteristic properties of MgO.

CaO belongs to the group of alkali metal oxide as well as MgO. However, Tsuchida et al. reported that CaO hardly gave butadiene in the conversion of ethanol [15]. Furthermore, hydroxylapatite, whose typical chemical formula is Ca₁₀(PO₄)₆(OH)₂, has both acid and base sites, however it gave butadiene with low selectivity [15]. In contrast with CaO, as mentioned above, MgO alone catalyzed the ethanol conversion to butadiene, realizing that the

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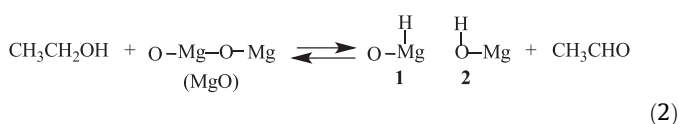
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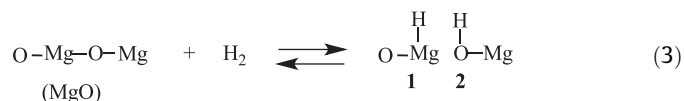
Scheme 1.

characteristic properties of MgO itself have a part in the formation of butadiene. On the basis of this concept, we proposed the catalyst reaction cycle over MgO as shown in Scheme 2, which comprises four key reaction steps (Step-1 - Step-4) [14].

According to Step-1 in Scheme 2, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is oxidized to acetaldehyde (CH_3CHO) over MgO (Eq. (2)). Thus, MgO induces the reversible heterolytic dissociation of C–H and O–H bonds in $\text{CH}_3\text{CH}_2\text{OH}$ molecules and proceeds to generate hydrogen atom species **1** and **2**.

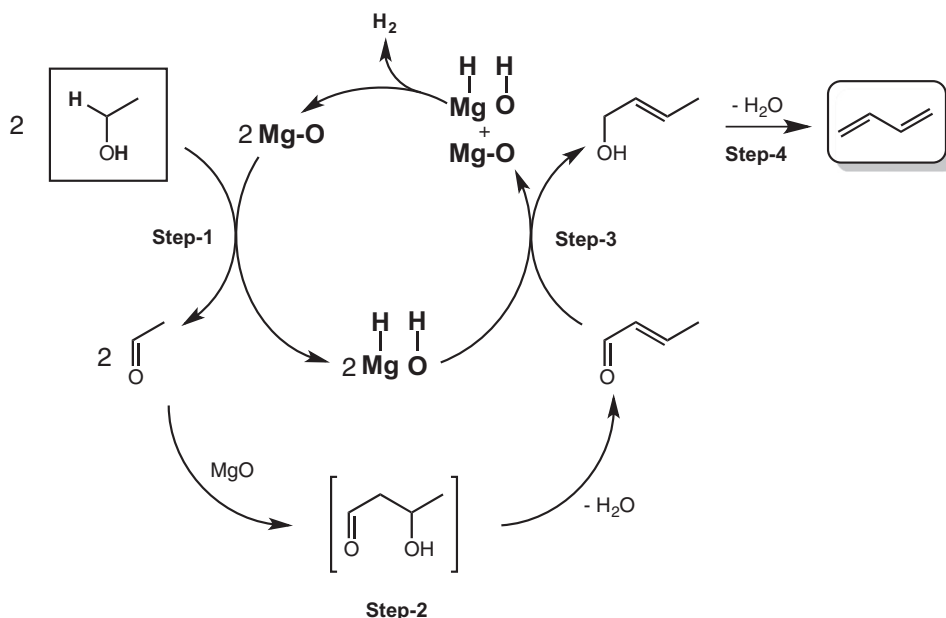
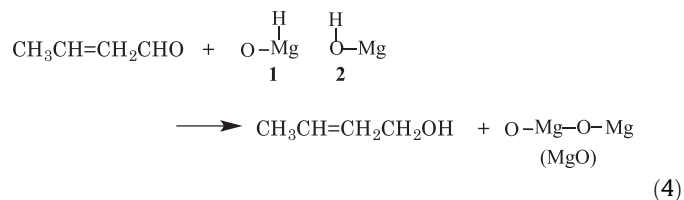


Eq. (2) depends on the evidence that MgO induces the reversible heterolytic dissociation of the hydrogen molecules and proceeds to generate hydrogen atom species **1** and **2** (Eq. (3)) [16,17]. This reversible heterolytic dissociation expressed by Eq. (3) was analogically applied to the conversion of $\text{CH}_3\text{CH}_2\text{OH}$ to CH_3CHO concomitant with the formation of hydrogen atom species **1** and **2** on MgO. In the reaction cycle shown in Scheme 2, hydrogen is possibly formed by the reverse reaction in Eq. (3), during the formation of butadiene from ethanol.



In Step-2, acetaldehyde (CH_3CHO) is converted to crotonaldehyde ($\text{CH}_3\text{CH}=\text{CHCHO}$). This conversion has been described as an aldol condensation reaction. The mechanism includes the formation of acetaldol by the condensation of two acetaldehyde molecules followed by dehydration of the aldol to the crotonaldehyde. In fact, it has been reported that MgO acts as a solid base catalyst for acetaldehyde conversion to crotonaldehyde [18].

In Step-3, crotonaldehyde reacts with hydrogen atom species **1** and **2** (Eq. (2)) to afford crotyl alcohol concomitant with MgO (Eq. (4)). In contrast to MgO, CaO cannot heterolytically dissociate hydrogen, indicating that hydrogen atom species like species **1** and **2** are not formed over CaO in the conversion of ethanol to butadiene.



Scheme 2. Reaction cycle for 1,3-butadiene formation from ethanol over MgO.

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