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Hydrogenation of lower alkenes and conjugated diene catalyzed by Ga_2O_3

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ABSTRACT

Hydrogenation of lower alkenes such as ethylene, propylene, and 1-butene proceeded over gallium oxide (Ga_2O_3). The rate of the hydrogenation was faster in the order of ethylene $\gg$ propylene > 1-butene over Ga_2O_3. Ga_2O_3 also showed the activity for hydrogenation of 1,3-butadiene where 1,4-addition of hydrogen to 1,3-butadiene mainly took place to give 2-butenes as main products. The formation rate of hydrogenated products depended on the amounts of H_2 and alkenes adsorbed on Ga_2O_3. This implies that the hydrogenation proceeds on the basis of the Langmuir–Hinshelwood mechanism.

1. Introduction

Activation of molecular hydrogen on solid surface is one of the most fundamental elementary steps in various chemical reactions such as hydrogenation of carbon–carbon unsaturated bond. Hydrogenation of alkenes and conjugated dienes catalyzed by various metals (platinum group metals, Ni and Co etc.) and transition metal oxides such as Cr_2O_3 [1], TiO_2, V_2O_5, MnO, Fe_2O_3, Co_3O_4 [2], ZnO [3–6], alkaline earth metal oxides (MgO, CaO, BaO, and SrO) [7–9], La_2O_3 [10,11], ZrO_2 [2,12–17], Al_2O_3 [18] and ThO_2 [11,19] have been investigated. Kokes and co-workers investigated the interaction of alkenes with molecular hydrogen on ZnO, and reported heterolytic cleavages of H_2 and C–H bond [3–6]. Hattori and co-workers reported that hydrogen molecule is adsorbed on heterogeneous basic catalysts such as alkaline earth metal oxides and La_2O_3 to form H^+ and H^- [7–11]. It has been generally applicable participation of heterolytically dissociated H^+ and H^- in the hydrogenation [20]. In addition to hydrogenation of alkenes, dissociatively adsorbed H^+ (M–OH) and H^- (M–H) also hydrogenate CO on MgO, La_2O_3, ZrO_2, and ThO_2 [20]. On the other hand, Kondo and co-workers reported that dissociatively adsorbed hydrogen forming Zr–H and Zr–OH species on the ZrO_2 did not react with gaseous ethylene [17]. They proposed that H_2 was activated on (or in the vicinity of) the site on which ethylene was already preadsorbed as a π-bonded species and preadsorbed π-bonded ethylene was found to be hydrogenated by gaseous H_2 to 'side-on' adsorbed ethane followed by a transformation into the more stable 'end-on' adsorbed ethane.

On the basis of FT-IR spectra, Collins et al. have reported that dissociatively-adsorbed hydrogen atoms (Ga–H^- and Ga–OH^+) are found to be formed on the surface of gallium oxide (Ga_2O_3) via heterolytic adsorption of hydrogen molecule [21,22]. Pan et al. also reported that hydrogen is dissociatively adsorbed to form H^+ and H^- on Ga_2O_3 by using FT-IR and DFT calculations [23]. Recently, we found that Ga_2O_3 also showed activity for the photocatalytic reduction of CO_2 in the presence of H_2 as a reductant [24,25]. CO was selectively produced at room temperature and ambient pressure under photo-irradiation. The amount of evolved CO depended not only on the amounts of CO_2 but also on the amounts of H_2 adsorbed on Ga_2O_3, which indicates that chemisorbed species of both CO_2 and H_2 are involved in the photocatalytic reduction of CO_2. FT-IR spectra showed that CO_2 adsorbed to form bidentate and monodentate bicarbonate and H_2 adsorbed dissociatively to form Ga–H^- and Ga–OH^+. We proposed that the dissociatively-adsorbed hydrogen on Ga_2O_3 reduced the monodentate bicarbonate to the bidentate formate under photoirradiation. The bidentate formate, which was an intermediate in the photocatalytic reduction, decomposed to CO. Hydrogenation of other molecules such as alkenes and dienes with molecular hydrogen is expected to take place over Ga_2O_3, because, on the surface of Ga_2O_3, Ga–H^- and Ga–OH^+ is generated from molecular hydrogen as well as MgO and these species (Ga–H^- and Ga–OH^+) showed activity for the photoreduction of CO. However, up to now, there is no report on the hydrogenation of alkenes and dienes over Ga_2O_3.

In this study, we report that hydrogenation of various lower alkenes and diene such as ethylene, propylene, 1-butene and 1,3-butadiene with molecular hydrogen takes place over Ga_2O_3. This is the first report of hydrogenations over Ga_2O_3.

2. Experimental

Ga_2O_3 was synthesized by adding aqueous solution of $Ga(NO_3)_3 \cdot xH_2O$ (Koujundo Chemical Laboratory Co. Ltd., 99.999%) to 25 mass% NH_3 aqueous solution to produce $Ga(OH)_3$. The precipitated gel was filtered under vacuum and washed with distilled

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water. The gel was then dried at 353 K for 24 h, followed by calcination at 1073 K for 6 h. The calcined sample was assigned to β-Ga_2O_3 phase (distorted hexagonal close-packed structure) based on X-ray diffraction (XRD) patterns. The Brunauer–Emmett–Teller (BET) specific surface area was 17 $m^2\,g^{-1}$.

The hydrogenations of lower alkenes and 1,3-butadiene with molecular hydrogen were carried out in a closed recirculation reactor connected to a vacuum line having a dead volume of 180.3 ml, 0.5 g of a Ga_2O_3 catalyst was used. Prior to reaction, Ga_2O_3 was evacuated for 0.5 h at 773 K and pretreated with 8 kPa of O_2 for 1 h at 773 K, followed by evacuation for 15 min at the same temperature. H_2 was purified by passage through 4A molecular sieves at 77 K. Lower alkenes (ethylene, propylene, and 1-butene) and 1,3-butadiene was purified by vacuum distillation at 77 K. Premixed gas of alkene (100 μmol) or 1,3-butadiene with H_2 (100 μmol) was circulated over Ga_2O_3. The reaction temperature of hydrogenation of lower alkenes was 373 K. Hydrogenation of 1,3-butadine was examined at 473 K. The products were analyzed using an on-line gas chromatograph (TCD, Shimadzu GC-8A) equipped with a column packed with Unicarbon A-400, and He was used as the carrier gas.

3. Results and discussion

Figure 1 shows the time dependence of the amount of alkanes in hydrogenation of lower alkenes with H_2 and the initial formation rate of alkanes over Ga_2O_3. The lower alkenes were hydrogenated to the corresponding alkanes. The rate of the hydrogenation was faster in the order of ethylene ≫ propylene > 1-butene over Ga_2O_3. This order is well accorded with those over heterogeneous basic catalysts such as MgO and CaO [7–9].

Figure 2 represents the time dependence of the amount of butenes and *n*-butane in the hydrogenation of a conjugated diene (1,3-butadiene) with H_2. 1,3-Butadiene was mainly hydrogenated to *trans* and *cis*-2-butens and a trace amount of *n*-butane was detected. This result indicates that the hydrogenation rate of monoenes is much different from that of conjugated diene, in other words, conjugated diene (1,3-butadiene) undergo hydrogenation much faster than monoenes (butenes). This result also indicates that 1,4-addition of hydrogen atoms took place over Ga_2O_3 in contrast to 1,2-addition which is commonly observed for conventional hydrogenation catalysts such as transition metals and transition metal oxides [7–9].

Hattori and co-workers reported that the hydrogenation over heterogeneous basic catalysts like alkaline earth oxides has characteristic features which distinguish basic catalysts from conventional metallic hydrogenation catalysts [7–11,20,26]. In the cases of alkaline earth metal oxides, 1,3-butadiene undergoes hydrogenation at 273 K, and the products of diene hydrogenation consist exclusively of monoenes with no alkanes being formed at 273 K. Hydrogenation of 1,3-butadiene mainly yields 2-butenes. These characteristic features of basic catalysts are basically similar to those of Ga_2O_3. Hattori and co-workers demonstrated that MgO was active and highly selective for the hydrogenation of 1,3-butadiene to *cis*-2-butene, during which H_2 maintained its molecular identity by using NMR and mass spectra. Both H atoms in a H_2 molecule are incorporated into one hydrogenated molecule [7–9]. On the basis of above features in hydrogenation of alkenes over basic catalysts, they proposed the reaction mechanism of hydrogenation of 1,3-butadiene in which anionic intermediates are involved. In this proposed mechanism, at first, hydrogen adsorbed dissociatively on the surface of metal oxide to form H^+ and H^-. Then, H^- attacks 1,3-butadiene to form the allyl anion of the *trans*-form which takes place either interconversion to form *cis*-allyl anion or addition of H^+ to form butenes. Since the electron density of

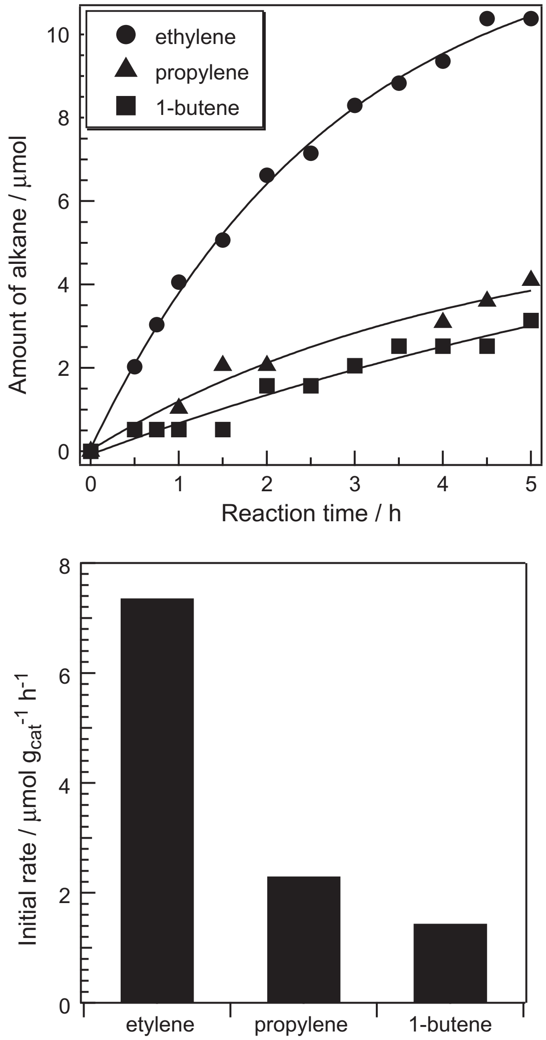


Figure 1. The time dependence of the amount of alkanes in the hydrogenation of lower alkenes with H_2 and the initial formation rate of alkanes over Ga_2O_3. Reaction temperature: 373 K, alkene (100 μmol) and H_2 (100 μmol).

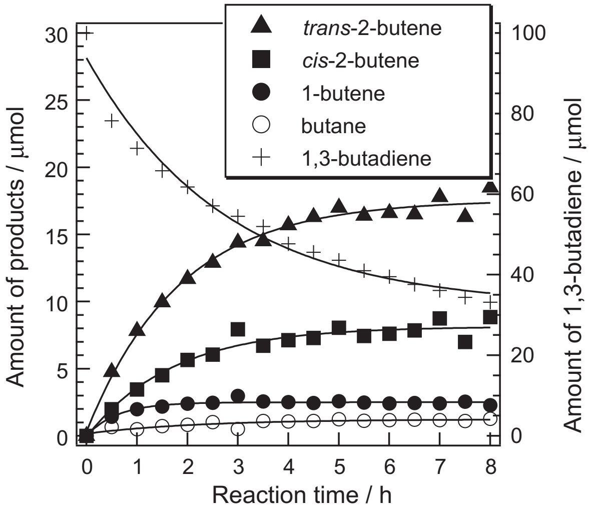


Figure 2. The time dependence of the amount of butenes and butane in the hydrogenation of 1,3-butadiene with H_2. Reaction temperature: 473 K, alkene (100 μmol) and H_2 (100 μmol).

the allyl anions is the highest on the terminal C atom, the positively charged H^+ selectively adds to the terminal C atom to complete 1,4-addition of H atoms to yield 2-butene. Because alkyl anions are less stable than allyl anions, a large difference in the reactivity between dienes and monoenes results from difficulty of alkyl anion formation compared to allyl anion formation. A similar feature in 1,3-butadiene hydrogenation over Ga_2O_3 and alkaline earth metal oxides suggests that both anionic intermediates and heterolytically dissociative-adsorbed hydrogen (H^+ and H^-) involved in the reaction mechanism of 1,3-butadiene hydrogenation over Ga_2O_3 as well as MgO (Scheme 1). However, a detailed reaction mechanism is now under investigation and will be reported in the near future.

The variations of the activity of Ga_2O_3 with the evacuation temperature for the hydrogenation of ethylene and the isomerization of 1-butene were measured to examine the nature of the active sites on Ga_2O_3 (Figure 3). The highest activity for hydrogenation of ethylene was observed after evacuation at 773 K. On the other hand, in the case of isomerization of 1-butene, the optimum evacuation temperature was 1173 K. This value was remarkably higher than those for the isomerization of 1-butene over MgO which is a typical basic catalyst. It was reported that the activities for hydrogenation of ethylene over MgO, CaO, SrO, and BaO reached the maxima for values of evacuation temperatures at 1373, 1073, 1273, and 1270 K, respectively [7–9]. These values were considerably higher than those for the isomerization of 1-butene which were 873, 873, 1073 and 1073 K, respectively. These temperatures are also higher than 773–873 K for the esterification [27], the polymerization [28] and the H_2–D_2 exchange reaction [29]. These facts strongly suggest that the active sites for hydrogenation of alkenes over alkaline earth metal oxides are different from those for isomerization of 1-butene, esterification, polymerization or H_2–D_2 exchange reaction. It has been believed that the active sites for hydrogenation on alkaline earth oxides are metal cation–O^{2-} ion pairs having low coordination number like Mg^{2+}_{3c}–O^{2-}_{3c} pairs (c denotes the coordination number of metal cation or oxygen anion), because such highly unsaturated sites are formed by the evacuation and removal of carbon dioxide at high temperatures [7–9,30,31].

In the case of Ga_2O_3, the optimum evacuation temperatures for hydrogenation of ethylene and isomerization of 1-butene were different as well as alkaline earth metal oxides. On the other hand, the optimum evacuation temperature for hydrogenation of ethylene was considerable lower than that for isomerization of 1-butene. Moreover, even after the evacuation at 1173 K, the activity for isomerization of 1-butene on Ga_2O_3 was much lower than that of MgO evacuated at 873 K. Moreover, Ga_2O_3 did not show any detectable activity for isomerization of 1-butene when evacuated at 773 K which was the temperature of the highest activity for the hydrogenation of ethylene. In the case of MgO, CO_2 completely poisoned the active site for both isomerization of 1-butene and hydrogenation of ethylene. In contrast, in the case of Ga_2O_3, CO_2 reduced only about a half of the activity for isomerization of 1-butene and 20% of the activity for hydrogenation of ethylene (Figure S1). These results indicate that the hydrogenation on Ga_2O_3 proceeds on different sites from those for isomerization and that basic sites on Ga_2O_3 was not active sites for hydrogenation of ethylene.

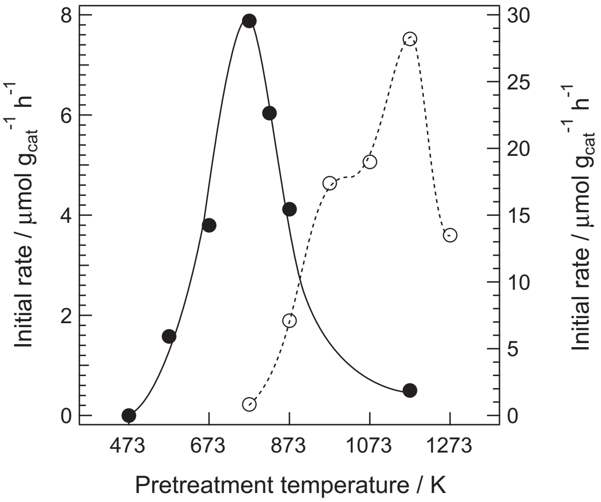
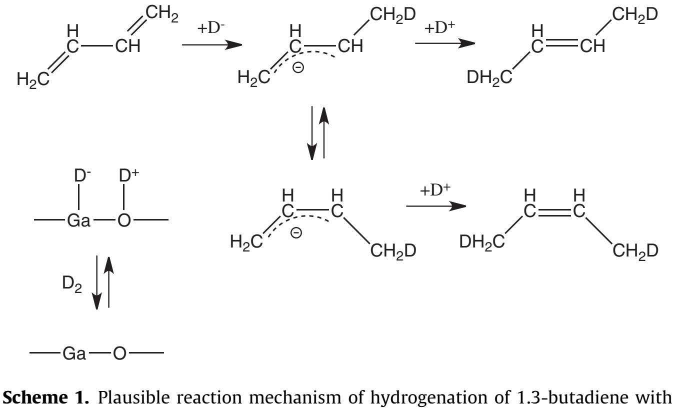


Figure 3. Effect of evacuation temperature of Ga_2O_3 on the activities in hydrogenation of ethylene (●) and isomerization of 1-butene (○). Reaction temperature: 473 K for hydrogenation of ethylene, 343 K for isomerization of 1-butene, Composition of reactants: ethylene (100 μmol) and H_2 (100 μmol) for hydrogenation of ethylene, 1-butene (100 μmol) for isomerization of 1-butene.

Figure 4 shows the dependence of adsorbed amount of ethylene and hydrogen over β-Ga_2O_3 against evacuation temperature. For both ethylene and hydrogen, the adsorbed amounts increased with a rise in evacuation temperature. In the case of hydrogen, the largest adsorbed amount was observed at 673 K and maintained up to



Scheme 1. Plausible reaction mechanism of hydrogenation of 1.3-butadiene with D_2 over Ga_2O_3.

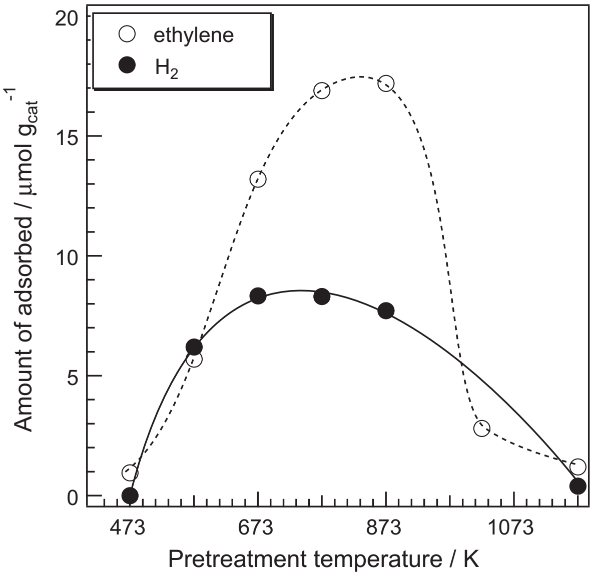


Figure 4. Effect of evacuation temperature of Ga_2O_3 on the amount of adsorbed H_2 (●) and etylene (○). The amount of hydrogen adsorption was measured at the reaction temperature (373 K).

873 K. On the other hand, in the case of ethylene, the adsorbed amount reached a maximum around 773 K. Therefore, a relatively-large amount of hydrogen and ethylene adsorbed over Ga_2O_3 evacuated at 773 K. According to Figures 3 and 4, the initial rate of ethylene hydrogenation depends on the amount of adsorbed hydrogen and ethylene. This implies that the hydrogenation of ethylene would proceed on the basis of the typical Langmuir–Hinshelwood mechanism. We have found that the adsorption isotherm of H_2 on β-Ga_2O_3 after the adsorption of ethylene is inconsistent with the conventional adsorption isotherm of H_2 on β-Ga_2O_3. Therefore, at present, we assume that a part of hydrogen adsorbed competitively on Ga_2O_3 with lower alkanes. The adsorption behaviors of lower alkenes and H_2 and the conformation of the adsorbed lower alkenes and H_2 species on β-Ga_2O_3 are now under investigation.

4. Conclusion

Hydrogenation of lower alkenes (ethylene, propylene, and 1-butene) to the corresponding alkanes proceeded over β-Ga_2O_3. The rate of the hydrogenation was faster in the order of ethylene ≫ propylene > 1-butene over Ga_2O_3. Ga_2O_3 also showed the activity for hydrogenation of 1,3-butadiene and 1,4-addition of hydrogen to 1,3-butadiene mainly took place to give 2-butenes as main product. The highest activity for hydrogenation of ethylene on Ga_2O_3 was observed after evacuation at 773 K, whereas the highest activity for isomerization of 1-butene was observed after evacuation at 1173 K. The active sites for hydrogenation on Ga_2O_3 are different from those for isomerization and basic sites of Ga_2O_3 is not active for hydrogenation. The initial rate of ethylene hydrogenation depends on the amounts of chemisorbed hydrogen and ethylene, which indicates that the hydrogenation of ethylene on Ga_2O_3 involves two adsorbed species, that is, H_2 and ethylene. This implies that the hydrogenation proceeds on the basis of the Langmuir–Hinshelwood mechanism.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2012.04.052.

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