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Hydrogenation behavior of propyne on supported Eu–Pd and Yb–Pd bimetallic catalysts with anomalous hydrogen uptake

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Abstract

The hydrogenation of propyne over SiO_2-supported lanthanide (Ln: Eu or Yb)–palladium bimetallic catalysts was studied at 203–273 K, especially concerning the hydrogenation behavior with considerable hydrogen uptake. Upon introduction of Eu or Yb onto Pd surfaces by the reaction of 5 mass % Pd/SiO_2 with the lanthanide metal dissolved in liquid ammonia, the ability of hydrogen uptake by the catalyst appeared during the hydrogenation of propyne. When the mixed gases, propyne and hydrogen, were brought into contact with $Ln–Pd/SiO_2$, considerable hydrogen uptake occurred, followed by hydrogenation to simultaneously form propene and propane. Pd/SiO_2-catalyzed propyne hydrogenation showed different product selectivity, in which negligible hydrogen uptake was observed. This indicates a mechanism different from that for $Ln–Pd/SiO_2$. $Ln–Pd/SiO_2$ showed remarkable synergetic effects between the lanthanide and palladium metal involving anomalous hydrogen uptake and hydrogenation behavior. The presence of adsorbed propyne on the catalyst surface was important to induce a promoting effect towards rapid hydrogen uptake with subsequent propyne hydrogenation. It seems quite certain that the hydrogenation on $Ln–Pd/SiO_2$ predominantly proceeds through a reaction path using hydrogen taken up by the catalyst.

Keywords: Lanthanide; Palladium; Bimetallic catalyst; Hydrogen uptake; Hydrogenation of propyne

1. Introduction

There has been increasing interest in the properties of lanthanides (Ln) and their related compounds as heterogeneous catalysts [1–3]. By using the dissolution of Eu and Yb in liquid ammonia [4], we have developed methods for preparing novel catalysts containing lanthanides, and have demonstrated that they exhibit specific catalytic properties [5–15].

Lanthanide–palladium bimetallic catalysts obtained when Eu or Yb metals dissolved in liquid ammonia react with 5 mass % Pd/SiO_2 show anomalous hydrogen uptake during propene hydrogenation [16]. It has been proven that the appearance of synergetic effects between the lanthanide and palladium metal is involved in such an interesting hydrogenation behavior. The amounts of hydrogen taken up by $Yb–Pd/SiO_2$ ($Yb/Pd=0.43$) exceed 12 in H/Pd ratio, assuming that all the hydrogen is absorbed by palladium. This hydrogen uptake is not due to the solubility of hydrogen in palladium and/or lanthanide in the catalyst. The hydrogen taken up is highly reactive, and is completely consumed for the propene hydrogenation. Extensive kinetic studies indicate that the hydrogenation on $Ln–Pd/SiO_2$ proceeds exclusively through a reaction path using the hydrogen taken up by the catalyst by a rate-limited uptake.

To provide information regarding the factors responsible for the hydrogenation reactions, the influence of the support materials, Pd particle size and dispersion in the supported Pd catalysts as precursors have been studied [17]. Differences in reactants have been also proven to be important factors in determining the hydrogen uptake and subsequent hydrogenation behavior. When ethyne is used as a reactant, there is no indication of any hydrogen uptake heretofore. However, for the hydrogenation of propyne, the occurrence of considerable hydrogen uptake by $Ln–Pd/SiO_2$ was observed. In the present study, we undertook to investigate the effects of lanthanide metal overlayer on the hydrogen uptake and related hydrogenation behavior of

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propyne over SiO_2-supported lanthanide–palladium bimetallic catalysts.

2. Experimental

2.1. Materials

Eu and Yb ingot (99.9%) were obtained from Shin-Etsu Chemical Co. Ltd. and used in the form of turnings or granules. SiO_2 (380 m^2 g^{-1}) was the commercially available Degussa Aerosil 380. $PdCl_2$ (99.9%; Rare Metallic Co. Ltd.) was commercially obtained and used without further purification. Ammonia (Iwatani Ind. Ltd.) was dried through a calcium oxide column and subsequently through a sodium hydroxide column before use. Propyne was of research purity and further purified by triple distillation.

2.2. Procedures of catalyst preparation and catalytic reactions

The preparation of Pd/SiO_2 and $Ln–Pd/SiO_2$ were basically carried out according to previous studies [16,17]. SiO_2-supported Pd catalyst was prepared by impregnating SiO_2 with aqueous solutions of $PdCl_2$ to get 5 mass % palladium, followed by drying and reduction at 623 K with hydrogen.

The 5 mass % Pd/SiO_2 that had been reduced was placed in a Schlenk tube containing a solution of liquid ammonia (15–20 cm^3) at 198 K. Eu or Yb were added to the Pd catalyst suspended in liquid ammonia with vigorous stirring. Upon dissolution of the lanthanide metal in liquid ammonia, a blue homogeneous solution was immediately formed, characteristic of the solvated electrons [4]. The blue color gradually disappeared as a result of the reaction of the dissolved lanthanide metal with the Pd catalyst. On disappearance of the blue color, the reaction tube was allowed to warm up to room temperature and the excess ammonia pumped out leaving SiO_2-supported Eu–Pd and Yb–Pd bimetallic catalysts. All sample preparation steps were carried out in an atmosphere of dry nitrogen without exposure to air, otherwise the catalysts became unreactive.

The catalytic reactions were performed on a recirculation reactor constructed of Pyrex glass that was equipped with a mercury manometer. Prior to the reaction the catalyst was subjected to evacuation treatment at 293–1073 K for 2 h, set at 203–273 K reaction temperature and then the hydrogenation was initiated by admitting H_2 and C_3H_4. The reacting gas in the system was periodically collected by a gas sampler and analyzed by a Shimazu TCD gas chromatograph (GC) with an active alumina column. The gas composition during the reaction was always determined by considering the mass balance between the quantities of propyne, propene and propane evaluated by GC and the changes in pressure in the gas-phase. Since the uptake of propene and propane by the catalyst was negligibly small to be identified by manometric techniques, the hydrogen uptake was estimated from differences between the quantities of the hydrogen obtained from the drop in pressure and the hydrogen used in the formation of propene and propane products. The hydrogenation rates were evaluated by measuring the rate of conversion of propyne.

3. Results and discussion

3.1. Hydrogenation behavior of propyne over $Ln–Pd/SiO_2$

The hydrogenation was carried out at 203 K by admitting mixed gases of propyne (17 Torr) and hydrogen (34 Torr). The 5 mass % Pd/SiO_2 used here was active for the hydrogenation of propyne. The reaction proceeded in the same manner as the hydrogenation behavior observed for normal Pd catalysts [18] (Fig. 1); thus, propyne was highly selectively hydrogenated to propene without any induction period, followed by the successive conversion of propene into propane. Ln/SiO_2 exhibited very low or negligible activity under similar conditions [19,20].

Upon introduction of the lanthanide metal onto the Pd surface, the catalytic properties of $Ln–Pd/SiO_2$ were markedly changed (Fig. 2). $Yb–Pd/SiO_2$ (Yb/Pd=0.67) showed the rapid hydrogen uptake over a period of ca. 10 min in the very beginning of the reaction, followed by the hydrogenation of propyne to steadily yield propene with abrupt formation of propane. However, further formation

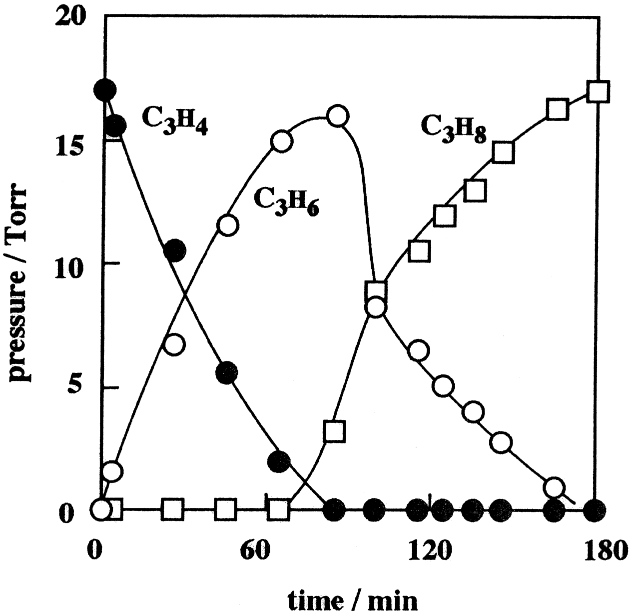

Fig. 1. Hydrogenation of propyne at 203 K over 5 mass % Pd/SiO_2. The catalyst (0.05 g) was evacuated at 623 K for 2 h before the reaction. $P(C_3H_4)=17$ Torr, $P(H_2)=34$ Torr.

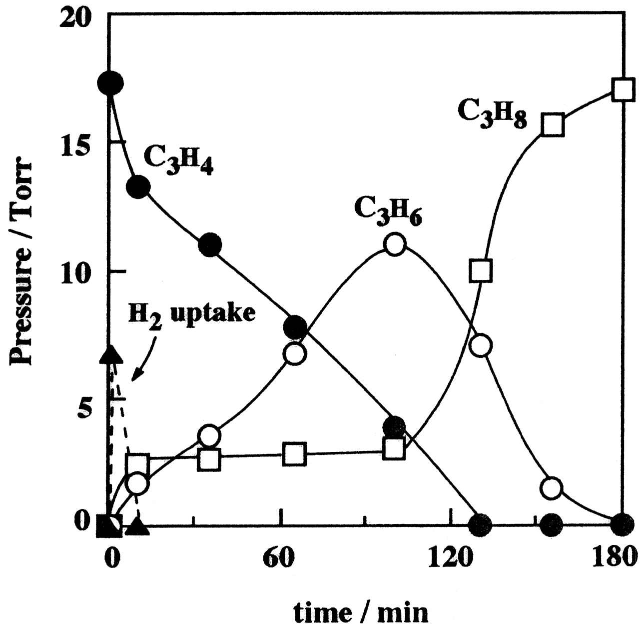

Fig. 2. Hydrogenation of propyne at 203 K over Yb–Pd/SiO_2 (Yb/Pd=0.67). The catalyst (0.05 g) was evacuated at 623 K for 2 h before the reaction. $P(C_3H_4)=17$ Torr, $P(H_2)=35$ Torr.

of propane scarcely occurred until the conversion of propyne to propene was completed at reaction times of ca. 120 min. No reaction of propyne with hydrogen was observed during the initial hydrogen uptake; there was an obvious induction period for the hydrogenation. The Eu-promoted Pd catalysts exhibited behavior similar to the Yb-promoted ones in the composition ranges investigated. Such a hydrogenation mode has been similarly observed for the hydrogenation of ethene, propene, butene and butadiene on Ln–Pd/SiO_2 or Ln–Pd/Al_2O_3 [17]. Unlike Pd/SiO_2 and Ln/SiO_2, Ln–Pd/SiO_2 showed considerable hydrogen uptake with induction period during the hydrogenation. These results strongly indicate that the hydrogenation of propyne proceeds by a mechanism associated with the hydrogen taken up. It seems quite certain that the difference in such a hydrogenation behavior between Pd/SiO_2 and Ln–Pd/SiO_2 is due to the occurrence of anomalous hydrogen uptake.

From an analysis of the material balance among hydrogen and propyne as reactants, and propene and propane products (as shown in Fig. 2), it has been proved that the hydrogenation of propyne proceeds by consuming both the hydrogen taken up by the catalyst and the hydrogen in the gas-phase. However, this does not necessarily imply that propene and propane are produced through separate reaction paths, considering rapid hydrogen uptake-extracting cycles as shown later.

The catalysts transiently contain significant amounts of hydrogen species able to efficiently hydrogenate propyne as a means of extracting hydrogen. In particular, the initial hydrogenation activity using hydrogen taken up is too high for the hydrogenated propene product to desorb with subsequent replacement by propyne; the hydrogenation proceeds to propane without a break as illustrated in Fig. 2. Such hydrogen species taken up by the catalyst were all consumed for hydrogenating propyne in the initial reaction step and subsequently, the steady hydrogenation continued; the hydrogenation in the latter half of the reaction occurred similarly to that observed for Pd/SiO_2 (Fig. 1).

3.2. Influence of co-existent propyne on hydrogen uptake

There was no indication of hydrogen uptake by the catalyst even when Ln–Pd/SiO_2 was brought into contact with only hydrogen at 203 K. A very important feature of the present catalyst systems is that the hydrogen uptake occurred only in the presence of propyne, in which the effect of a co-existent gas was obviously recognized as observed for olefin and diene [16,17]. As shown in Fig. 3, Yb–Pd/SiO_2 (Yb/Pd=0.43) was exposed to hydrogen at 38 Torr and 203 K for 30 min, followed by propyne (17 Torr) addition. The addition of propyne resulted in rapid hydrogen uptake by the catalyst; the adsorbed propyne preferentially induces the hydrogen uptake. For the reaction of propyne and hydrogen, there was also a definite induction period. The remarkable uptake of hydrogen by the catalyst was also observed during this induction period. However, when the sequence of hydrogen and propyne addition was reversed (propyne was circulated over Yb–

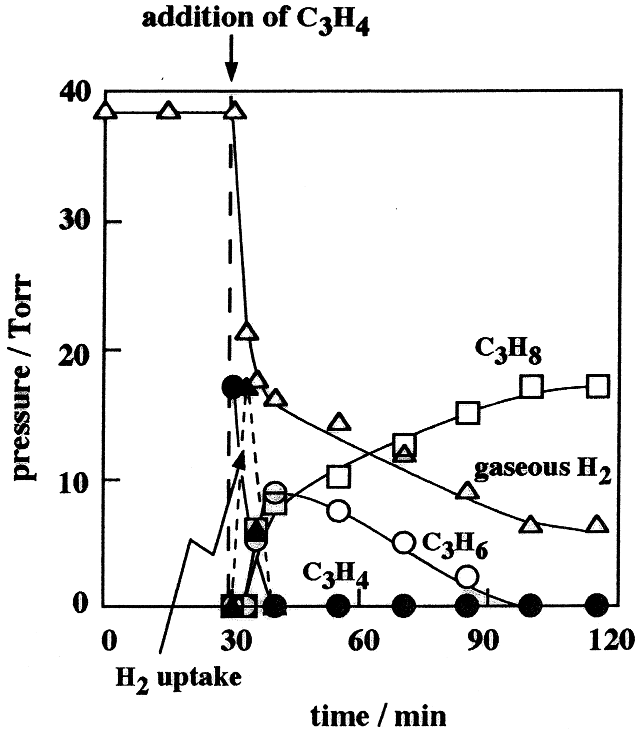

Fig. 3. Effect of co-existent propyne on the hydrogenation behavior. An arrow indicates the introduction of propyne. Yb–Pd/SiO_2 (Yb/Pd=0.43) (0.05 g) was evacuated at 633 K for 2 h before the reaction. The hydrogenation was carried out at 203 K by introducing hydrogen (38 Torr) and subsequently propyne (17 Torr).

Pd/SiO$_2$ at 203 K for 30 min, followed by hydrogen addition), no hydrogen uptake was observed at all and normal hydrogenation of propyne occurred like that shown in Fig. 1.

Such phenomena observed only in the presence of propyne do not imply that hydrogenated intermediates whose surface concentration builds up before substantial desorption of the propene and propane products. This is because the carbon balance among propyne, propene and propane was always maintained during the reaction; hence the possibility of a decrease in pressure due to its disappearance from the gas-phase can be ruled out. Since the hydrogenation with such hydrogen uptake was similarly observed at a reaction temperature of 273 K, condensation of the reactant gases into pores of the catalyst is hard to consider. Thus, the co-existent propyne plays an important role in the rapid initiation of hydrogen uptake with subsequent hydrogenation processes, in which a phenomenon similar to spillover may exist [21]. Vannice characterizes perylene in Pt black/Ce–Y–zeolite as bridges between the Pt black and zeolite of the catalyst facilitating hydrogen migration [22,23]. We have observed the fact that the hydrogen uptake is strongly affected by presence of such a second gas as ethene, propene, butene and buta-1,3-diene [16,17].

To further examine how the hydrogen uptake is affected by presence of propyne, the hydrogenation of propyne (17 Torr) over Yb–Pd/SiO$_2$ (Yb/Pd=0.67) was carried out at 203 K with a large excess of hydrogen. When all of the propyne reactant was hydrogenated to propane, only propyne of 17 Torr was introduced into the reaction system to rerun the hydrogenation. As shown in Fig. 4, the hydrogenation with hydrogen uptake was similarly observed in each run. That the hydrogen uptake was again observed upon introduction of additional propyne leads to speculations of continuous occurrence of hydrogen uptake with subsequent rapid addition processes in the hydrogenation process. However, the hydrogenation activity for the second run was low compared to that for the first one and the amounts of hydrogen taken up decreased with runs. Moreover, after the hydrogenation of propyne on Yb–Pd/SiO$_2$ was carried out at 203 K for about 10 min, the reaction system was evacuated at the reaction temperature for 30 min, followed by addition of mixed gases of propyne and hydrogen again (Fig. 5). Although the hydrogenation activity entirely decreased, the hydrogenation of propyne with hydrogen uptake was similarly reproduced. This observation strongly indicates that the hydrogenation on Ln–Pd/SiO$_2$ always occurs with hydrogen uptake in which cycles of rapid hydrogen uptake and subsequent hydrogenation by consuming it are effectively operative.

For the separate constituent, Pd/SiO$_2$ or Ln/SiO$_2$, neither hydrogen uptake nor unusual hydrogenation behavior was observed under similar reaction conditions. Thus the present lanthanide–palladium bimetallic system is

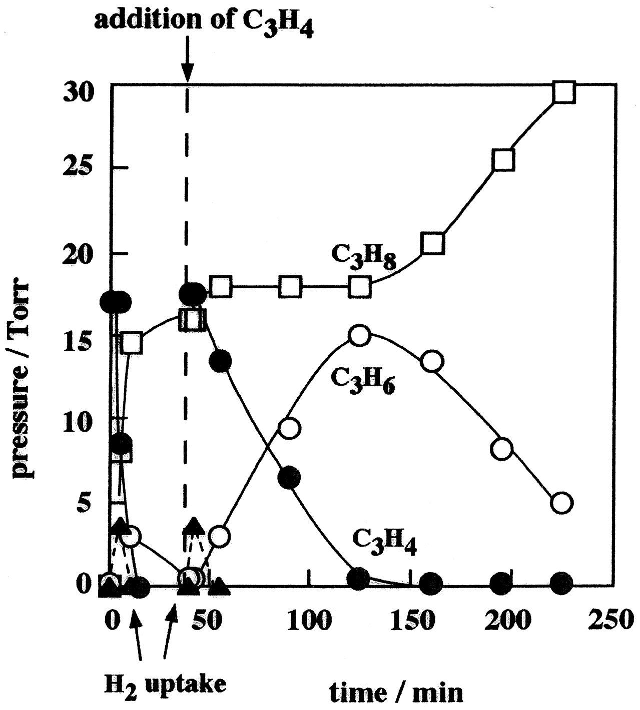

Fig. 4. Function of co-existent propyne during the hydrogenation over Yb–Pd/SiO$_2$ (Yb/Pd=0.67). The catalyst (0.05 g) was evacuated at 623 K for 2 h before the reaction. After the hydrogenation of propyne (16 Torr) with hydrogen (90 Torr) was completed at 203 K, only propyne (17 Torr) was introduced to the reaction system again.

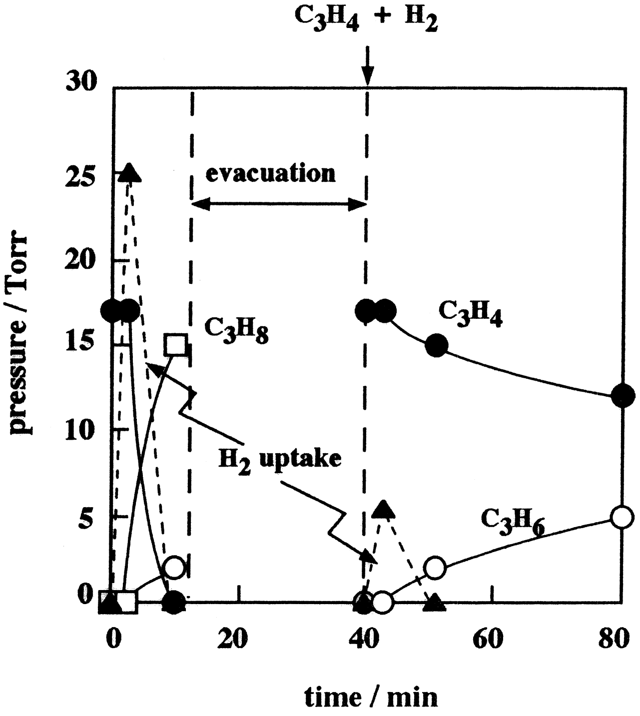

Fig. 5. Repeated hydrogenation of propyne at 203 K over Yb–Pd/SiO$_2$ (Yb/Pd=0.67). The reaction system was evacuated in the course of hydrogenation, followed by reintroduction of propyne (17 Torr) and hydrogen (34 Torr). The catalyst (0.05 g) was evacuated at 623 K for 2 h before the reaction.

an interesting example of synergism involved in hydrogenation behavior with an enhanced ability for hydrogen uptake. The existence of some synergetic effects between lanthanide and palladium metals rather than individual component elements constitutes active sites for the hydrogenation with considerable hydrogen uptake. However, substantial reasons as to how such synergism induces the hydrogen uptake and as to where the hydrogen species are accepted on/in the catalyst have not been clarified yet.

The rates of hydrogenation of propyne over Yb–Pd/SiO_2 showed a negative dependence on the hydrogen pressure and a positive dependence on the propyne pressure, which was very similar to that observed for the hydrogenation of propene with hydrogen uptake [16]. For the hydrogenation of acetylene during which there is no indication of hydrogen uptake at all, the reaction kinetics on Yb–Pd/SiO_2 give a first-order dependence of hydrogen, and are almost independent of acetylene pressure [17].

In addition, the thermal pretreatment of Ln–Pd/SiO_2 under vacuum conditions, before the reaction, affected the catalytic behavior. For the catalyst pretreated at a lower temperature near 293 K, no hydrogen uptake was observed and besides, the slow hydrogenation occurred without any induction period. The rates of hydrogen uptake and hydrogenation varied markedly with changes in evacuation temperature of Ln–Pd/SiO_2 and they showed a tendency to increase in the range of about 293 to 800 K. The hydrogenation activity of Yb–Pd/SiO_2 (Yb/Pd=0.43) evacuated at 623 K increased above 50-fold relative to that for the catalyst evacuated at 293 K. The rates of hydrogen uptake by Yb–Pd/SiO_2 varied markedly with the evacuation temperatures. As depicted in Fig. 6, the temperature dependence of the hydrogen uptake well corresponded to that of the hydrogenation activity. The number of active sites on Ln–Pd/SiO_2 which was evaluated from CO chemisorption also increased with increasing the evacuation temperature from 293 to 723 K. As reported previously for Ln–Co [9,12], Ln–Ni [5,6,9,13,14], Ln–Cu [5,6,15] and Ln–Ag [5–7,15] bimetallic systems, we have demonstrated that such thermal treatments result in rearrangement of surface morphology or structure, leading to the appearance of enhanced catalytic activity. For Nd/Cu(111) [24] and Yb/Ni(100) [25,26], that the overlayer-to-intermetallic transition occurs by heating at elevated temperatures has been proven.

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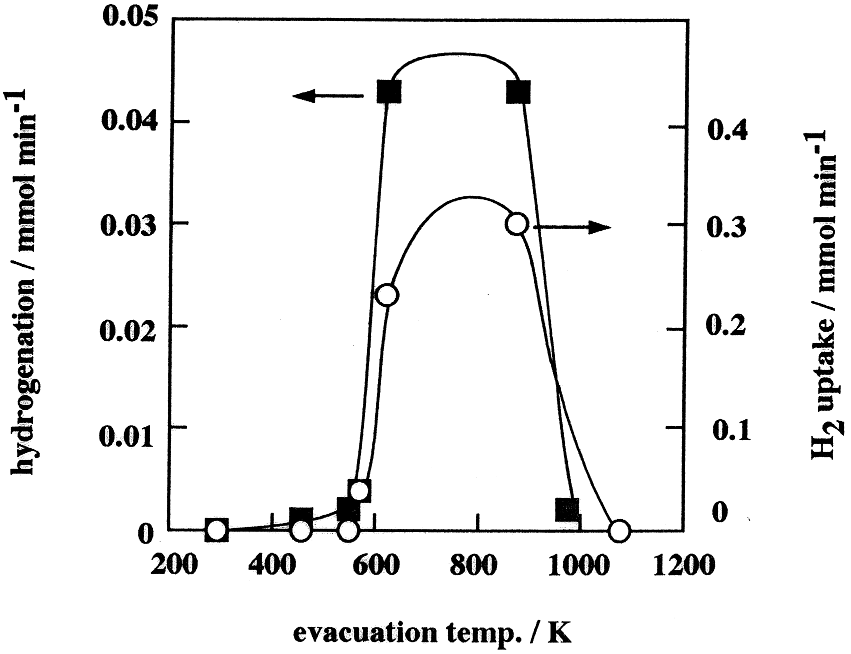

Fig. 6. Dependence of hydrogen uptake and hydrogenation activity on evacuation temperatures of Yb–Pd/SiO_2 (Yb/Pd=0.43). The catalyst (0.05 g) was evacuated at prescribed temperatures for 2 h before the reaction. The reaction was carried out at 203 K by introducing a mixed gas of propyne (17 Torr) and hydrogen (34 Torr).

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