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Formation of C4 species in the deactivation of a Pd/SiO_2 catalyst during the selective hydrogenation of acetylene

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Abstract

The deactivation characteristics of Pd/SiO_2 in the selective hydrogenation of acetylene were correlated with changes in the amount of the C4 species produced. The amounts of butenes produced changed in parallel with the catalyst activity, indicating that the rate limiting step for butene production was the same as that for acetylene hydrogenation. On the other hand, the amount of 1,3-butadiene produced changed, showing a maximum with catalyst deactivation because 1,3-butadiene is an intermediate in the sequential reaction process which involves both the production and consumption of 1,3-butadiene. This was verified by a simultaneous TG/reaction experiment showing that 1,3-butadiene was a precursor of green oil. The catalyst showed a self-regenerative behavior in its activity and the amounts of C4 species produced during the early stage of deactivation because two opposite factors, which contributed to either the lowering or the promotion of activity, were involved in the process. A specific type of polymer species, produced during the initial period of deactivation, is proposed to be responsible for the promotion of catalyst activity.

Keywords: Acetylene hydrogenation; Pd catalyst; Deactivation; Green oil; 1,3-Butadiene; Butene

1. Introduction

Supported Pd catalysts are typically used in the selective hydrogenation of acetylene to remove acetylene from the ethylene stream from naphtha crackers [1–3]. In addition to hydrogenation, acetylene undergoes hydropolymerization, leading to the formation of not only various C4 compounds but higher hydrocarbons (green oil) on the catalyst surface. The influence of green oil on ethylene selectivity has been studied by several groups [4–7]. The amount of the oligomeric species deposited on the catalyst increases with decreasing H_2/acetylene ratio, resulting in decreased overall activity and ethylene selectivity [5]. In particular, surface coverage by hydrogen was found to be a crucial factor in catalyst deactivation by accumulated green oil [6,8]. Although the composition of green oil and the deactivation characteristics of catalysts have been investigated [5,9–11], the mechanism of deactivation during acetylene hydrogenation remains largely unknown.

Several authors have proposed a reaction mechanism that involves oligomer formation from dissociatively adsorbed acetylene [6,12–15]. Sarkany et al. [6] considered C4 formation to be an indication of green-oil production, but only the influence of total C4 species on catalyst deactivation was discussed. Recently, butadiene has been proposed to be a precursor candidate because it is volatile, easily polymerized, and is formed in appreciable amounts during acetylene hydrogenation [10,16]. In order to design improved catalysts that produce smaller amounts of green oil, it is necessary to understand the effects of the production of different C4 species during the deactivation process.

In this study, the deactivation mechanism was further investigated by introducing a novel method for verifying the precursor of green oil. In order to clarify the role of individual C4 species, a specially-designed apparatus combining a thermogravimetric instrument and gas chromatography (TG–GC) was used for *in situ* observation. *In situ* changes in catalyst properties, including deactivation rates, catalyst weight, and the amounts of C4 species produced, were monitored under different conditions of process parameters, including reaction temperature and H_2/acetylene ratio.

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2. Experimental

2.1. Catalyst preparation

One weight percentage of Pd/SiO$_2$ catalyst was prepared using silica (D11-10 obtained from BASF, surface area = 145 m^2/g, pore volume = 0.42 ml/g, average pore diameter = 11.5 nm, particle size = 85–120 μm) as a support and Pd(NH$_3$)$_4$(OH)$_2$ as a Pd precursor by an ion exchange method reported in a previous study [17]. After drying overnight at 110 °C, the catalyst was calcined in air at 300 °C for 2 h, and then reduced in H$_2$ at 300 °C for 1 h prior to use. The Pd dispersion of catalyst, estimated by H/Pd ratio, is 0.45 after reduction at 300 °C [17].

2.2. Reaction tests and temperature programmed analysis (TGA)

For acetylene hydrogenation, 0.05 g samples of catalyst were tested under atmospheric condition in a quartz reactor. The reactant stream contained 4.1% acetylene in ethylene flowing at either 31 ml/min or 42 ml/min (space time: 4.19×10^{-3} min or 3.10×10^{-3} min), the H$_2$/acetylene ratio was 1 or 2, and the temperature was varied between 50 °C and 110 °C. The products were analyzed with an on-line GC (HP model 6890 series with FID) using a capillary column (HP-AL/S).

In situ experiments to monitor changes in the catalyst weight during reaction were conducted using a specially-designed apparatus combining a TG and GC. Catalyst weight was thermogravimetrically measured with a Magnetic Suspension Balance (Rubotherm) during the catalyst deactivation process. A 0.05 g sample of catalyst was loaded in a basket made of stainless-steel tubing (OD = 13 mm, ID = 10 mm, height = 9 mm) welded with a stainless-steel grid. The flow rate of the reactant stream was 31 ml/min, and the H$_2$/acetylene ratio and temperature were fixed at 1 °C and 70 °C, respectively. Contrary to the case of reaction tests conducted using a quartz reactor, a large fraction of the reactant stream bypassed the catalyst through the space between sample basket (OD = 13 mm) and the inner wall (ID = 24 mm) of TG instrument. The products were analyzed with an on-line GC and catalyst weights were simultaneously measured.

3. Results

3.1. Deactivation rates versus the H$_2$/acetylene ratio

Fig. 1 shows the deactivation of the catalyst during a reaction carried out at a fixed H$_2$/acetylene ratio of 1 and different temperatures (Pd/110 denotes Pd/SiO$_2$ used for the reaction at 110 °C). The absolute conversion increases with reaction temperature, as shown in Fig. 1(a). Catalyst activity, represented by the conversion normalized to the initial value, was monitored as a function of the total amount of converted acetylene, such that the deactivation characteristics could be compared based on the same load of the reaction. The catalyst was deactivated slowly during the initial period, but was deactivated at higher rates when the total amounts of converted acetylene were larger than *ca.* 0.025 mol. Catalyst deactivation in the later stage was accelerated when the reaction temperature was decreased from 110 °C to 70 °C [18].

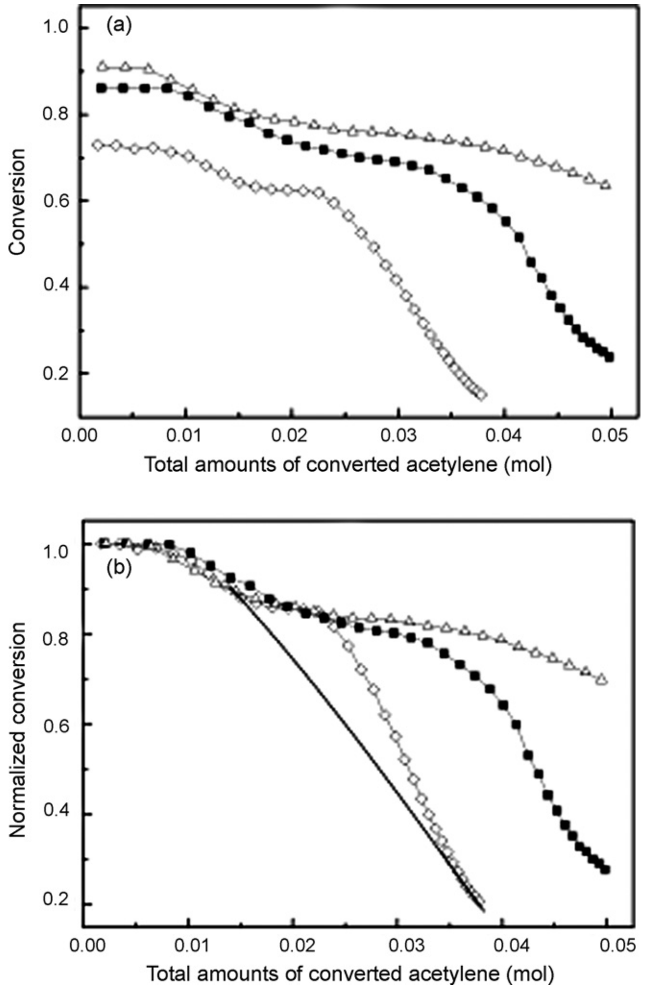

Fig. 1. Changes in the catalyst activity as a function of the total amounts of converted acetylene (H$_2$/acetylene = 1): Pd/110 (△); Pd/90 (■); Pd/70 (◇): (a) actual conversion; (b) normalized conversion.

Fig. 2 shows the mol fractions of different C4 species produced in a reaction at 70 °C. The amounts of butene species, including 1-butene, *trans*-2-butene, and *cis*-2-butene, decreased with the amounts of converted acetylene, in parallel with catalyst activity. On the other hand, the amounts of 1,3-butadiene started to increase when the amounts of converted acetylene were larger than 0.020 mol, but eventually decreased in the later stage after reaching a maximum at *ca.* 0.025 mol.

Fig. 3(a) shows simultaneous changes in the activity and weight of the catalyst during the reaction process, as measured using a combined TG/reactor unit. Due to the bypass of the reactant stream in the TG/reactor unit, the initial conversion, 50%, was lower than the 73% obtained in the reaction tests and displayed in Fig. 1(a) for Pd/70. The activity decreased together with an increase in catalyst weight, suggesting that the accumulation of green oil is a major contributor to the deactivation [5,6,9]. The gradients of the TG curve, which represent the rates of green-oil formation, were compared with