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Modified Pd catalysts for the selective hydrogenation of acetylene

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ABSTRACT

This article reviews our previous studies to develop high performance catalysts for acetylene hydrogenation. Ethylene selectivity of Pd catalysts in acetylene hydrogenation was improved by adding Si, metal oxides showing SMSI behavior, and either Ag or Cu as promoters. The promoter effect was further enhanced by maximizing the interactions between Pd and added promoters. Chemical vapor deposition was used for the addition of Si, high-temperature reduction for the SMSI metal oxides, and a surface redox (SR) for Ag and Cu. Si modified the Pd surface geometrically, SMSI metal oxides modified Pd both electronically and geometrically, and Ag modified Pd largely electronically. Cu added by SR modified Pd electronically to a small extent, but preferentially decorated the low-coordination sites of Pd such that the ethylene selectivity of the optimum catalyst was significantly promoted from that of Pd, while its activity remained comparable to that of Pd. The sensitivity of ethylene selectivity to the surface structure of Pd was demonstrated using model catalysts containing uniform-sized Pd particles in either cubic or spherical shapes. The three stage deactivation of the Pd catalyst and the self-regenerative behavior in early stages of deactivation were also investigated.

1. Introduction

An ethylene stream from a naphtha cracker unit typically contains about 0.1–1% of acetylene as an impurity, which is required to be removed to less than 5 ppm because it poisons the catalyst in ensuing ethylene polymerization processes and eventually degrades the quality of the produced polyethylene [1,2]. Acetylene impurities are usually removed by two methods, that is, adsorption with zeolite [3] and conversion to ethylene by selective hydrogenation using Pd catalysts [2], the latter more commonly being used.

Two factors are the keys to the assessment of this process. One is the ethylene selectivity [4], i.e., the fraction of ethylene produced by acetylene conversion, and the other is the catalyst lifetime which is limited by green oil deposition during the reaction [5].

Various additives, such as Ag, Ni, Cu, Pb, Tl, Cr, and K, have been reported to improve the performance of Pd catalysts, especially in achieving a high selectivity for ethylene production [6–12]. The role of additives, or selectivity promoters, is generally considered to be derived from two factors: geometric [8,13] and electronic [6,11]. For example, Leviness et al. [8] reported the promotion of ethylene selectivity upon Cu addition, which they proposed to be due to a geometric effect. That is, the insertion of Cu into the Pd matrix decreases the number of multi-coordination sites of the Pd responsible for the dissociative adsorption of acetylene and suppresses the formation of beta phase Pd hydride as well; both are damaging to ethylene selectivity. On the other hand, Huang et al. [6] reported an improved selectivity on Ag-promoted Pd catalysts, suggesting that an increase in the Pd d-band electron density upon Ag addition was responsible for the selectivity enhancement.

To design a novel catalyst with improved performance in acetylene hydrogenation, it is necessary to consider the reaction mechanism for acetylene hydrogenation, which consists of several reaction paths, as shown in Fig. 1 [14]. Path I is the partial hydrogenation pathway of acetylene to ethylene, which is either desorbed as the major gaseous ethylene product (Path II) or further hydrogenated to ethane (Path III). Consequently, ethylene selectivity can be improved by promoting Path II and suppressing Path III, for which two methods are typically used in industrial processes. One is to add a moderator chemical to the reaction stream, e.g., CO, which adsorbs more strongly on Pd than ethylene and, consequently, facilitates ethylene desorption from the catalyst surface (Path II) [15]. The other is to maintain a low H_2/acetylene ratio in the feed such that the catalyst surface is deficient in hydrogen concentration, thus the full hydrogenation of ethylene (Path III) is retarded [16,17]. Path IV, allowing the direct full hydrogenation of acetylene to ethane, is insignificant at high acetylene coverage and low partial pressures of hydrogen [18], which is the case in most industrial processes. The triply adsorbed species, ethylidyne, had been suggested as an intermediate in Path IV [8,18–20] but was

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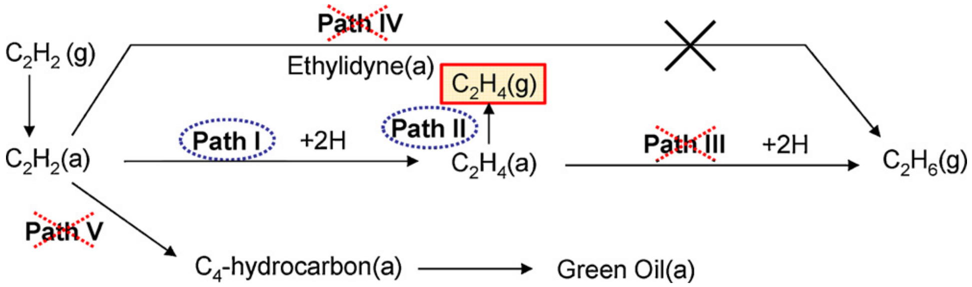

Fig. 1. Reaction paths of acetylene hydrogenation [14].

later verified to be a simple spectator of surface reactions [21,22]. Path V, which allows for the dimerization of the C_2 species, eventually leads to catalyst deactivation via the accumulation of green oil [23,24]. Path V also lowers the ethylene selectivity because it consumes acetylene without producing ethylene. Accordingly, the mechanism of acetylene hydrogenation indicates that, for improving ethylene selectivity and suppressing green oil formation, Paths I and II should be promoted while the other paths should be suppressed.

Our research efforts for the development of a high performance acetylene hydrogenation catalyst, both in ethylene selectivity and catalyst lifetime, focused on selectively manipulating the electronic and geometric structure of the Pd catalyst by incorporating new promoters [13,14,25–30], selectively depositing promoters on specific Pd surfaces [13,14,25–32], and controlling the shape of the Pd particles [33]: (1) Si was selectively deposited on Pd active sites over SiO_2 or Al_2O_3 support using a chemical vapor deposition (CVD) method as a geometric modifier, such that the number of multi-coordination sites of the Pd surface was effectively suppressed leading to the high ethylene selectivity [13,25] and a decrease in green oil formation [27]; (2) metal oxides exhibiting phenomenon similar to strong metal–support interaction (SMSI) were added to the Pd catalyst as a geometric and electronic modifier, such that the adsorption strength of reagents as well as multi-coordination sites of Pd surface were effectively controlled, leading to the high ethylene selectivity [14,26,30] and suppression of green oil formation [29]; (3) Pd sites were decorated with a promoter added by surface reduction method (SR), such that specific Pd structure responsible for lowering ethylene selectivity was effectively blocked [31,32].

This article reviews our previous studies based on the above three strategies.

2. Si-modified Pd catalysts prepared by selective CVD

2.1. Selective deposition of Si on the Pd surface

The Pd surface in Pd/SiO_2 was modified with Si deposited on the Pd surface by silane (SiH_4) decomposition and its catalytic performance in acetylene hydrogenation was investigated. Pd/SiO_2, used as a model catalyst, was prepared by an ion exchange method using $Pd(NH_3)_4(OH)_2$, and the Si-modified catalyst, Pd–Si/SiO_2, was prepared by selectively depositing Si on the Pd surface as previously reported [13]. 1% SiH_4/H_2 mixture was injected as pulses into the H_2 stream flowing through a reactor that contained the pre-reduced Pd catalyst and was maintained at 250 °C. The amount of deposited Si was controlled by the number of repetitive injections. After the Si deposition, the reactor was cooled to room temperature and the catalyst was exposed to O_2 for 1 h such that the Si species deposited on the Pd surface was oxidized.

2.2. Catalytic performance of Si-modified catalyst

The catalytic performance of the Si-modified Pd catalyst (Pd–Si/SiO_2) in acetylene hydrogenation was compared with that of an un-modified one (Pd/SiO_2) with respect to two key factors: ethylene selectivity and catalyst deactivation.

Fig. 2 shows typical results of acetylene hydrogenation obtained on Pd/SiO_2 and Pd–Si/SiO_2 over a wide conversion range [13]. Obviously, the ethylene selectivity increased when the catalyst was modified with Si, while acetylene conversion was slightly lowered upon Si addition. The added Si appears to be a promoter for ethylene selectivity rather than for the hydrogenation activity of the Pd catalyst.

The extent of catalyst deactivation by green oil formation was also analyzed for both catalysts [27]. Pd/SiO_2 and Pd–Si/SiO_2 were deactivated, with the same level of acetylene conversion and the reaction rates of both catalysts were plotted as normalized values to their initial reaction rates against the accumulated amounts of acetylene conversion in Fig. 3. Obviously, the catalyst deactivation was suppressed on Pd–Si/SiO_2 (b-1) compared to that on Pd/SiO_2 (a-1). Pd catalysts used in acetylene hydrogenation are deactivated largely due to the accumulation of green oil on the Pd active sites [34]. The above findings suggest that Si addition has a beneficial effect on the catalytic performance of the Pd catalyst in acetylene hydrogenation by increasing ethylene selectivity as well as decreasing green oil formation.

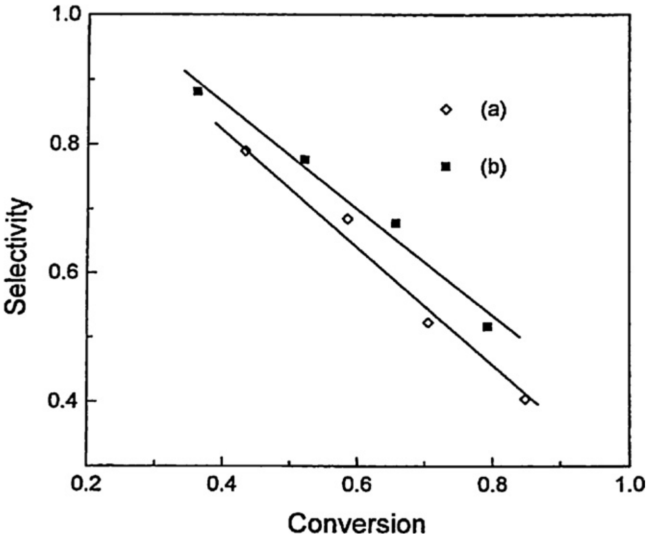

Fig. 2. Ethylene selectivity versus conversion in acetylene hydrogenation (H_2/acetylene = 2, T = 60 °C): (a) Pd/SiO_2; (b) Pd–Si/SiO_2 (Si/Pd = 0.095) [13].