Applied Catalysis A: General 360 (2009) 38–42

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Three-stage deactivation of Pd/SiO_2 and Pd-Ag/SiO_2 catalysts during the selective hydrogenation of acetylene

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ARTICLE INFO

Article history:
Received 6 November 2008
Received in revised form 26 February 2009
Accepted 26 February 2009
Available online 11 March 2009

Keywords:
Acetylene hydrogenation
Pd catalyst
Ag addition
Deactivation
Green oil
Formation mechanism

ABSTRACT

The deactivation of Pd/SiO_2 and Ag-promoted Pd/SiO_2 catalysts was monitored during their use in the selective hydrogenation of acetylene. Based on the analysis of green oil accumulated on the deactivated Pd/SiO_2 catalysts, it was proposed that the catalyst deactivation proceeded in three stages. In the initial stage (Stage I), a large amount of relatively light green oil was deposited on, or in the vicinity of, the Pd surface, but the catalytic activity decreased only slightly. As the deactivation proceeded (Stage II), the 1,3-butadiene that had accumulated on the Pd surface was polymerized to relatively heavy green oil, a part of which moved from the Pd surface to the support. In the later stage of deactivation (Stage III), catalytic activity was drastically decreased because catalyst pores were blocked and hydrogen diffusion was limited in the thick film of the relatively heavy green oil.

Although the initial activity of Ag-promoted Pd/SiO_2 was slightly lower than that of the unpromoted one, the amount of green oil deposited on the former catalyst was much smaller than that deposited on the latter. Consequently, the final stage of deactivation (Stage III) was not observed with Pd-Ag/SiO_2 during the reaction period of this study. Pd-Ag/SiO_2 showed Stage II, characterized by the transfer of green oil from the Pd to the support, at a period earlier than in the case of Pd/SiO_2, which additionally contributed to the slow deactivation of the former catalyst. The green oil that formed on the Pd-Ag/SiO_2 was more volatile and mobile than that formed on Pd/SiO_2, because the added Ag geometrically blocked multi-coordinated large ensembles of the Pd surface and also modified the Pd electronically such that the adsorption of 1,3-butadiene on the Pd became weaker than in the absence of promotion.

1. Introduction

Green oil, which is a major contributor to the deactivation of Pd catalysts in acetylene hydrogenation, has been studied extensively [1–7]. The carbonaceous deposits, which constitute green oil, modify catalytic performance by changing the catalyst surface properties: reducing the surface area [8], poisoning active sites [9], and limiting the diffusion of acetylene into the catalyst [10–12].

However, the above changes in the surface properties contribute to catalyst deactivation in different extents and in manners not necessarily proportional to the amounts of the deposits. For example, the initial activity of Pd was nearly preserved when the catalyst contained the deposits in amounts as large as 36 wt%, suggesting that the majority of active sites were still available for the reaction [7]. On the other hand, the activity was significantly lowered even by a small increase in the amounts of the deposits when the catalyst was in the later stage of deactivation [10–12].

Accordingly, the effect of the carbonaceous deposits on the activity should be investigated over the entire lifetime of the catalyst, i.e., from fresh catalyst to an almost dead one, such that their contribution to, and the underlying mechanism of, the deactivation is assessed according to the process period.

In the present study, we compared the deactivation behaviors of Pd/SiO_2 and Ag-promoted Pd/SiO_2 by simultaneously monitoring changes in catalyst activity and in the amounts of 1,3-butadiene, a known precursor of green oil [13], produced through the last stage of catalyst deactivation. The observed behaviors correlated with the properties of green-oil species that were deposited on the catalysts at different stages of deactivation. Finally, a mechanism that explains the role of Ag as a promoter for extending the lifetime of Pd/SiO_2 has been proposed based on the above results.

2. Experimental

2.1. Catalyst preparation

Pd/SiO_2 catalyst containing 1 wt% of Pd was prepared by an ion-exchange method using silica (surface area = 145 m^2/g) as a

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doi:10.1016/j.apcata.2009.02.044

support and $Pd(NH_3)_4(OH)_2$ as a Pd precursor [14]. Ag-promoted Pd catalyst was prepared by impregnating Pd/SiO_2 with an aqueous solution of $AgNO_3$. The atomic ratio of Ag/Pd was adjusted to 0.5. The catalysts were dried at 110 °C overnight and calcined in air at 300 °C for 2 h. All catalysts were reduced in H_2 at 300 °C for 1 h before being used for acetylene hydrogenation.

2.2. Reaction tests

A 0.06 g sample of the catalyst, contained in a quartz reactor, was used for acetylene hydrogenation at atmospheric pressure. The reactant stream contained 4.1% acetylene in ethylene flowing at 30 ml/min (space time: 4.33×10^{-3} min). The H_2/acetylene ratio was 1 and the reaction temperature was 90 °C. The products were analyzed using an on-line GC (HP model 6890 series with FID) equipped with a capillary column (HP-AL/S).

2.3. Green-oil analysis

An elemental analyzer (EA1110, CE Instrument) was used to measure the amounts of carbon and hydrogen contained in green oil deposited on the catalyst after use in the reaction test. Total amounts and types of green oil were also measured thermogravimetrically (TGA) with a Magnetic Suspension Balance (Rubotherm) in a 10% O_2/N_2 stream flowing at 40 ml/min. The temperature was raised from 25 °C to 700 °C at a rate of 5 °C/min. Differential thermogravimetric analysis (DTGA) results were obtained from the TGA curves by differentiating the latter with respect to temperature.

2.4. CO-IR

A 0.07 g sample of catalyst was pressed into a self-supporting disc 17 mm in diameter, placed in the IR cell with CaF_2 windows [15], reduced at 300 °C, and then exposed to 14.6 Torr of CO at room temperature for 5 min. The IR spectra of adsorbed CO were recorded (Midac 2100) after the removal of gaseous CO from the cell by evacuation.

3. Results

3.1. Deactivation behaviors

Fig. 1 shows changes in the activities of Pd/SiO_2 and Ag-promoted Pd/SiO_2 as a function of the reaction period, which are represented by the accumulated amounts of converted acetylene such that the deactivation characteristics could be compared based on the same load of the reaction [13,14]. Data obtained at the same time-on-stream for two sample catalysts have been connected by subsidiary lines. The activity of Pd/SiO_2 changed characteristically during the three reaction periods. That is, the activity remained nearly constant when the accumulated amounts of converted acetylene were smaller than 0.014 mol (designated as Period I). On the other hand, the activity drastically decreased when the accumulated amounts of converted acetylene were larger than 0.030 mol (designated as Period III). During the intermediate period (Period II), the activity decreased slightly. The activity of Pd-$0.5Ag/SiO_2$ decreased at an almost constant rate during the entire period of this study. As a result, a drastic decrease in the activity was not observed during Period III, which agreed with the well-known information that the lifetime of the Pd catalyst was extended by Ag promotion [16].

The amounts of 1,3-butadiene, a proposed precursor of green oil [13], were plotted versus the reaction period, as shown in Fig. 2. In the case of Pd/SiO_2, the amounts of 1,3-butadiene increased at relatively low rates during Period I, which was followed by an increase in the amounts that eventually showed a maximum during the next period of the deactivation process (Period II), and then decreased significantly during Period III. To the contrary, Pd-$0.5Ag/SiO_2$ produced smaller amounts of 1,3-butadiene that increased only slightly during Period II. The period required for producing the maximum concentration of 1,3-butadiene, marked in the figure, was shorter for Pd-$0.5Ag/SiO_2$, i.e., after the conversion of acetylene in the accumulated amounts of about 0.022 mol, than for Pd/SiO_2, which showed the maximum at 0.030 mol of converted acetylene.

3.2. Rates of green-oil formation

Fig. 3 shows the amounts of green oil deposited on the catalysts, obtained by EA and TGA, as a function of catalytic activity, which was represented by acetylene conversion in the deactivation process. The C and H contents of green oil, recovered from the catalysts after use for different periods, are also summarized in Table 1. In Fig. 3, solid and broken lines that connect TGA and EA data, respectively, show nearly the same correlations between the amounts of green oil and catalytic activity. During the initial period of the reaction (Period I), large amounts of green oil, about 34 wt%, were deposited on Pd/SiO_2, even though the conversion decreased slightly by 2%. These results indicate that the reaction successfully

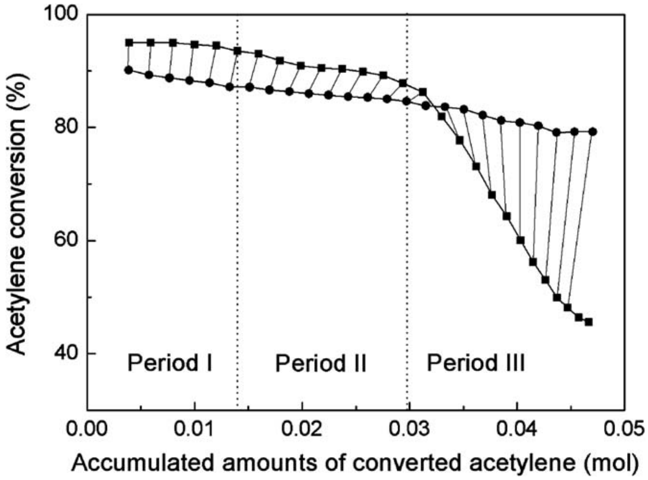

Fig. 1. Changes in the catalytic activity as a function of the accumulated amounts of converted acetylene on Pd/SiO_2 (■) and Pd-$0.5Ag/SiO_2$ (●).

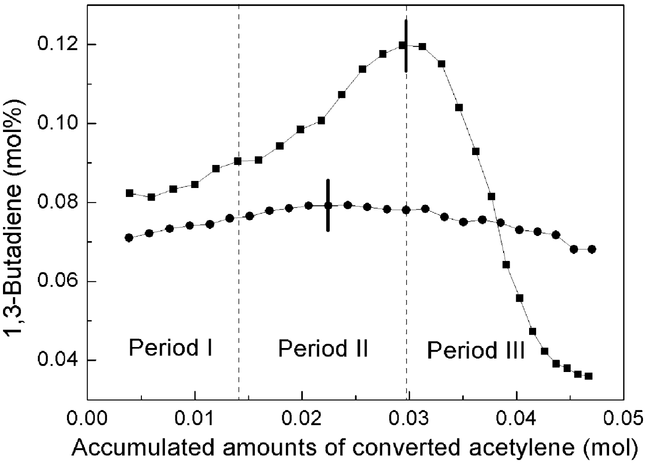

Fig. 2. Changes in the amounts of produced 1,3-butadiene as a function of the accumulated amounts of converted acetylene on Pd/SiO_2 (■) and Pd-$0.5Ag/SiO_2$ (●).