



Pd-Ag/Al₂O₃ catalyst: Stages of deactivation in tail-end acetylene selective hydrogenation



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ABSTRACT

The deactivation of a Pd-Ag/α-Al₂O₃ catalyst (2.5 mm in diameter, containing 0.03 wt.% Pd and 0.18 wt.% Ag) with egg-shell distribution was studied for acetylene selective hydrogenation. The reaction was performed in a fixed bed reactor using C₂H₂/C₂H₄/H₂ feed mixture (1:67.5:1.5 molar ratio). The long-term deactivation behaviour of the catalyst was studied by differential method of analysis using appropriate power law kinetics for the main reaction and catalyst decay. Based on the analysis of model results, it was proposed that the catalyst deactivation proceeded in two stages. The initial stage (Stage I) was relatively short (<20 h) and characterized by rapid catalyst deactivation, followed by second stage (Stage II) of much slower deactivation rate exhibiting a deactivation rate constant one order of magnitude smaller than Stage I. It was attributed to the dual role of carbonaceous deposits on catalyst that exhibited sequential activation and deactivation effects. The TG and FT-IR analysis of the spent catalyst revealed formation of aliphatic (soft) coke after about 100 h on stream.

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1. Introduction

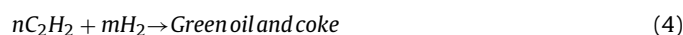
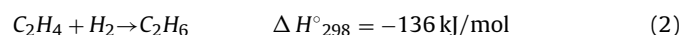
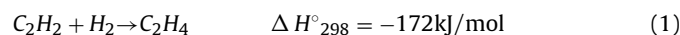
Acetylene selective hydrogenation is an important industrial process for the efficient removal of acetylene impurity from an ethylene stream. As acetylene is a poison for Ziegler-Natta catalyst that is used in down-stream polymerization process, its content must be reduced to 1–5 ppm range [1].

Commercially, acetylene selective hydrogenation can be performed based on two scenarios; namely front-end and tail-end; which depends on feed condition. A schematic diagram of a typical olefin plant is depicted in Fig. S1 in which front-end hydrogenation reactor was marked as location 1 and tail-end hydrogenation reactor was marked as location 2. Tail-end configuration is the most commonly implemented one in commercial plants worldwide. In front-end scheme, hydrogenation takes place before the removal of lighter components such as H₂, CH₄ and CO and the feed with high excess of hydrogen directly enters the reactors. In tail-end hydrogenation process, hydrogenation takes place after the removal of lighter hydrocarbons (H₂, CH₄ and CO) [2].

Since 1950's, monometallic palladium catalysts were used worldwide for acetylene selective hydrogenation processes. As

palladium had limited selectivity and poor long-term stability, bimetallic catalysts were introduced in 1980s in which palladium was promoted with another metal such as Si, Ag, Ti, Cu, Th, Au, Pb, Co, Ni, K, Ce, Nb, Re and Zn, among which Ag is the most common one. The main role of promoter by which selectivity could be improved is isolation of Pd active sites and decreasing coordination number of Pd atoms (geometric effect), alloying with promoters (electronic effect) or reducing hydride transfer (kinetic effect) [3–6].

Generally, in tail-end acetylene selective hydrogenation, which is the target process of the present research, the following four reactions take place [7]:



Reaction (1), as an exothermic irreversible one, is the desired reaction whereby acetylene is selectively hydrogenated to ethylene. Simultaneously, by reaction (2), ethylene could be hydrogenated to ethane which leads to an unwanted reduction of the ethylene selectivity. Moreover, the formation of heavy hydrocarbons, collectively known as "green oil", from acetylene and hydrogen is illustrated in reaction (4). Green oil is a major

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Nomenclature

Symbols

a	Catalyst activity
C_i	Concentration of species i (mol/m^{-3})
F_i	Flow rate of species i (mol h^{-1})
k	Reaction rate constant ($\text{m}^6 \text{kg}^{-1} \text{mol}^{-1} \text{h}^{-1}$)
k_d	Catalyst deactivation rate constant (h^{-1})
r'_i	Rate of disappearance for species i per mass of catalyst ($\text{mol kg}^{-1} \text{h}^{-1}$)
t	Time (h)
TOS	Time on stream (h)
W	Catalyst weight (kg)
V_{ads}	Volume adsorbed ($\text{cm}^3 \text{g}^{-1}$)
V_g	Molar volume of gas at STP (cm^3)
X	Conversion

Subscript

A	Acetylene
A_0	Acetylene in feed
B	Hydrogen

Greek symbols

ε	Volume expansion factor
\mathcal{H}	Hydrogen / acetylene molar ratio (mol mol^{-1})

contributor to the deactivation of Pd catalysts in acetylene hydrogenation [8,9].

Ahn et al. [10] studied the deactivation of Pd/SiO₂ and Ag-promoted Pd/SiO₂ catalysts during selective hydrogenation of acetylene. Based on the analysis of green oil accumulated on the deactivated Pd/SiO₂ catalysts, it was proposed that the catalyst deactivation proceeded in three stages. In the initial stage, a large amount of relatively light green oil was deposited on, or in the vicinity of, the Pd surface, but acetylene conversion decreased only slightly. As the deactivation proceeded, 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 last stage, acetylene was drastically decreased because catalyst pores were blocked and hydrogen diffusion was limited in the thick film of the relatively heavy green oil.

Although green oil is considered as the main cause of deactivation of Pd-based catalysts, the trend in deactivation could be quite different from that of green oil formation and deposition. In the present work, the deactivation of Pd-Ag/Al₂O₃ catalyst during selective hydrogenation of acetylene is studied. Unlike previous works, the catalyst activity is considered instead of acetylene conversion in deactivation study. Due to the industrial importance of deactivation, the findings of the present research could be implemented for any commercial plant as it is based on catalyst activity which is a measurable parameter during plant operation.

2. Materials and methods

2.1. Chemicals

A commercial Pd-Ag/Al₂O₃ catalyst (2.5 mm in diameter), produced by Süd-Chemie, containing 0.03 wt.% Pd and 0.18 wt.% Ag was used. Feed cylinders containing acetylene-ethylene gas mix (1.5 mol% C₂H₂ with C₂H₄ as balance), hydrogen (purity 99.9 mol%) and nitrogen (purity 99.9 mol%) were supplied from Pars Havaye Alborz and used as reactant or diluent gases.

2.2. Catalyst characterization

BET method was used in order to determine the surface area of the catalyst. At first, the sample was heated up to 300 °C in nitrogen. Then 0.5 g of the sample was filled in a reaction vessel and connected with the measure device (Nova 2200, Quantachrome). Gaseous nitrogen was added into the vessel after cooling down to 77 K in a Dewar filled with liquid nitrogen. Afterwards the pressure drop was measured that corresponds to the adsorbed nitrogen, the amount of which was used to determine the BET surface area from the slope of BET equation.

In order to determine palladium active sites, CO chemisorption was used. The catalyst sample was pretreated in glass reactor with a flow of 50 ml min⁻¹ hydrogen and 400 °C for 15 min. Then the reactor was connected to the chemisorption apparatus (BELCAT, type A) and cooled down to 50 °C in a 50 ml min⁻¹ flow of helium. Afterwards, a pulse of 1.009 ml CO was introduced in the reactor which was repeated every 1 min. A thermal conductivity detector (TCD) recorded the CO-signals. CO is chemisorbed on palladium only and not on silver [11].

In order to investigate types of Pd adsorption sites, CO temperature-programmed desorption (CO-TPD) measurement was performed using BELCAT A apparatus. The catalyst was loaded in a micro-reactor, reduced at 150 °C in H₂ stream for 2 h, and purged with He at 150 °C for 1 h to remove adsorbed H₂ from the Pd surface. The catalyst was then exposed to CO at 40 °C, before the temperature was raised from 40 °C to 700 °C at a rate of 10 °C/min in He stream.

The analysis of metal penetration depth was performed with field emission scanning electron microscope (FE-SEM) using MIRA3 TESCAN apparatus. Each spherical pellet was polished on the top surface whereby half of the active Pd-egg shell was revealed. Then, the pellet was covered with Au layer and transferred into the microscope. The measurements were carried out under high vacuum and with an electron beam having a voltage of 15 kV. The depth of the Pd-layer was read out from FE-SEM pictures.

The thermo-gravimetric (TG) measurements was performed using Perkin Elmer SII apparatus (model: Diamond TG/DTA) in the temperature range 25–800 °C to characterize coke deposition. The temperature scanning rate was 5 °C/min.

Fourier transform infrared (FT-IR) spectra of the catalyst was used to determine coke chemical structure using Bruker spectrometer (model: Vertex 80). Self-supporting discs containing the catalyst sample was prepared with KBr by applying pressure. The discs were used for recording FT-IR spectra in wave length range 4000–400 cm⁻¹.

2.3. Reaction study

The catalyst performance for tail-end selective hydrogenation of acetylene was evaluated using a high-pressure fixed-bed reactor. A schematic diagram and brief explanation of the set-up is provided elsewhere [12].

Each catalyst sample diluted with the same size quartz was used in performance tests. At the beginning, the catalyst was reduced *in situ* with hydrogen for 4 h by heating from room temperature to 150 °C. Then the reactor was purged with nitrogen and cooled down to the reaction temperature. Feed mixture containing 1 mol% C₂H₂, 1.5 mol% H₂, 30 mol% N₂ and C₂H₄ as balance was introduced through mass flow controllers (BROOKS instrument SLA 5850). The feed and products were analyzed by an on-line gas chromatograph (Varian-CP-3800) equipped with CP-Al₂O₃/Na₂SO₄ column (length: 50m, column OD: 0.25 mm and column thickness: 4 μm). The apparatus was equipped with FID and TCD detectors, both operating at 1.6 bar (23psi) and 230 °C. The absence of heat

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