



Palladium–Tin nanocatalysts in high concentration acetylene hydrogenation: A novel deactivation mechanism

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ARTICLE INFO

Article history:

Received 30 March 2013

Received in revised form 19 December 2013

Accepted 23 December 2013

Available online 9 January 2014

Keywords:

High-concentrated acetylene

Tin-promoted catalyst

Deactivation

Isolated adsorption site

Green oil

Intermetallic

ABSTRACT

In the present study, tin-promoted Pd/MWNTs nanocatalysts were prepared via polyol method for further application in highly concentrated acetylene hydrogenation. Particle sizes decreased drastically with addition of tin, indicating a narrow particle size distribution. The particle sizes and the associated distribution remained constant, even after aging the nanocatalyst upon the reaction for a long time. Addition of tin to Pd catalysts showed good propensity towards the highly-stabilized catalysts, in particular, at the molar ratios of Sn/Pd more than 0.25 up to 1. To characterize the catalysts examined, TEM, XRD, TPR, XPS, SIM DIS, FTIR and TPO were applied. XPS and XRD experiments confirmed the formation of intermetallic compounds and Pd₂Sn alloy, respectively. The results showed that the presence of these structures on the catalyst surfaces were responsible for the higher catalytic performance, especially, for the catalysts with higher molar ratios of Sn/Pd. Also, a novel mechanism was proposed based on which the higher values of Sn/Pd were more unaffected in contrast to deactivation. This was attributed to the lower ability of the catalyst to dehydrogenate carbonaceous species, which in turn, decreased the spillovers of carbonaceous species from the catalyst surface to the support, increasing the life time of the catalyst.

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1. Introduction

Acetylene hydrogenation has attracted so much attention for many years, because the small traces of acetylene in ethylene derived from cracking are able to poison the polymerization catalysts [1–5]. The use of rich-ethylene feedstocks is known as a common industrial process, however, recently, some reports claimed the use of acetylene-rich feedstocks for ethylene production [6,7]. Hall et al. [6,7] applied methane as the main constituent of natural gas to acetylene, followed by hydrogenation of acetylene to produce ethylene, however, the main idea in this course was to produce liquid hydrocarbons. This process may be supposed as an important alternative route, because of the presence of abundant sources of methane. Mamadov et al. [8] also proposed a method by which highly concentrated acetylene streams were applied for subsequent hydrogenation to ethylene. As they found out, either fixed bed reactors or wash coated ones are suitable to hydrogenate acetylene selectively to ethylene. They preferred SiO₂, ZrO₂, Al₂O₃, TiO₂ or a mixture thereof as support and Cu, Co, Cr, K, Pt, Ru, Au, Ag as the metal sites.

Alumina-supported Pd catalyst is conventionally employed for acetylene hydrogenation reaction in spite of low ethylene selectivity

at high acetylene conversions and additionally, the formation of more values of green oil upon the reaction, decreasing the lifetime of the catalyst [5,9,10]. The addition of promoters such as Ag [1], Si [11], Ti [10] and Ni [12] may be helpful to increase the selectivity to ethylene and therefore, to subsequently decrease the green oil via suppression of the formation of by-products.

There are some reports regarding the use of tin promoter in hydrogenation reactions, however, it is usually applied as the main promoter in dehydrogenation reactions [13,14]. The unique characteristics of tin are probably attributed to the strong metal-support interaction (SMSI) and/or the alloy formation between tin and precious metal [15]. In other words, some geometric and electronic effects are of interesting importance for the enhanced performance of tin [16]. For instance, in the case of tin-promoted Pt catalysts, in geometric aspect, tin decreases the size of platinum ensembles, with which in turn, lower coke formation is expected. Furthermore, in electronic effects, tin could modify the electronic density of Pt due to positive charge transfer from Snⁿ⁺ species to Pt and the formation of different alloys of Pt–Sn. These modifications may be responsible for some changes in the heat of adsorption of different adsorbates, facilitating the reaction [16].

To the best of our knowledge, the main challenge in the course of hydrogenation of high concentration acetylene feedstocks is the formation of green oil, followed by the catalyst deactivation. Alkhawaldeh et al. [17] investigated the deactivation behavioral pattern of the zeolite-supported catalyst conversion of methane and acetylene or ethylene

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in the presence of hydrogen ($H_2/C_2H_2 = 2.5$). According to them, the catalyst was stabilized ca. 3 h, followed by a drastic decrease in acetylene conversion. Also, Trimm et al. [18] studied the catalytic behavior of Ni/SiO₂ in the oligomerization of acetylene using hydrogen with a volumetric ratio of H_2/C_2H_2 of 3. They observed a complete conversion of acetylene over a period of 5 h at 140 °C followed by a sharp decrease of acetylene conversion.

The positive role of the unique adsorption sites as isolated form on ethylene selectivity, in the course of acetylene hydrogenation has been already introduced by McLeod and coworkers [19–22]. The formation of isolated adsorption sites could occur on the catalyst surface by two different ways as described in the following. The first one is attributed to the formation of ordered intermetallic compounds [19,20]. These compounds have a well-defined homogeneous distribution of the active sites crystallized due to the covalent bonding between the transition metals and the promoter used [19]. According to what is mentioned above, one may conclude that the intermetallic compounds have single-phase materials, owing the structured isolated phases of Pd, whereas, alloys are composed of a mixture of metals, intermetallic compounds and/or non-metals, including more than one phase [20]. Kovnir et al. [19,20] could improve the ethylene selectivity and the lifetime of the catalyst in the selective hydrogenation reaction of acetylene using ordered Pd–Ga intermetallic catalyst.

Another effective method to enhance the number of isolated adsorption sites is via the carbonaceous overlayer formed on the metal surface upon the acetylene hydrogenation reaction. According to the literature [21,22], the presence of carbonaceous coverage could enhance the number of isolated adsorption sites, improving the ethylene selectivity by preventing the formation of by-products which in turn, could increase the lifetime of the catalyst. Since higher carbonaceous coverage could increase the number of isolated adsorption sites as those of non-competitive, the decrease of ethylidyne production and subsequently, further deactivation of the catalyst is expected [21,22].

In the present study, the investigation of the effect of tin as the promoter of Pd/MWNTs catalysts is of our interest. Herein, we make an attempt to study the deactivation behavior of tin-promoted Pd/MWNTs catalysts upon the highly concentrated acetylene hydrogenation reaction.

2. Material and methods

Multi-walled carbon nanotubes used as support, in this research, were synthesized via chemical vapor deposition (CVD) of methane over Co–Mo/MgO at 900 °C, followed by purification through washing in an aqueous solution of HCl and then, in HNO₃ solution to eliminate the impurities [23]. Afterwards, the resulting MWNTs were functionalized using sonication for 3 h in a mixture of sulfuric and nitric acids with volumetric ratio of 3:1, respectively.

Polyol method was applied to synthesize all the catalysts, according to what was reported elsewhere [24]. Briefly, aqueous solutions of metal precursors (PdCl₂, SnCl₂·2H₂O, Merck) were added to MWNTs dispersed in ethylene glycol (EG, Merck) under vigorous stirring. Afterwards, pH of the solution was adjusted to ca.12, followed by heating the mixture rapidly up to 140 °C under reflux conditions, while argon gas (30 cm³/min) was passed through it. After keeping the reaction mixture in the conditions mentioned for 3 h, the resulting products were filtered and dried in a vacuum oven at 90 °C for 4 h. The molar ratios of Sn to Pd of 1:0.1, 0.25, 0.5, 1 and 0.1 wt.% Pd loading for all of the samples were utilized, except for XRD and XPS analyses with a Pd loading of 5 wt.%.

In order to evaluate the catalytic activities of the catalysts, a stainless steel vertical reactor of 1/4 in. outer diameter was applied, containing 0.1 g catalyst powder diluted with SiC. The gas feedstock ($H_2:C_2H_2 = 2:1$) diluted with Ar (70%vol.) was introduced into the reactor with GHSV of ca. 33,000 h⁻¹. The reaction was carried out in the range temperature of 150–180 °C. To decrease the drawbacks resulting from the exothermic reaction, an oil bath, having large

thermal mass, was used. The gas concentration outlet of the reactor was measured by Shimadzu gas chromatography with an alumina packed column.

The conversion of acetylene and selectivity to ethylene and ethane in the hydrogenation reaction are defined as follows:

$$\text{Conversion (\%)} = \frac{F_{i,ac} - F_{o,ac}}{F_{i,ac}} \times 100$$

$$\text{Selectivity to ethylene (\%)} = \frac{F_{o,ey}}{F_{i,ac} - F_{o,ac}} \times 100$$

$$\text{Selectivity to ethane (\%)} = \frac{F_{o,ea}}{F_{i,ac} - F_{o,ac}} \times 100$$

in which the molar flow is abbreviated as F (mol/min), the subscripts “i” and “o” are assigned to the feed into and effluent of the reactor. Also, the subscripts “ac”, “ey” and “ea” stand for acetylene, ethylene and ethane, respectively.

Transmission electron microscopy (TEM) images were obtained using a CM-FEG-Philips, having an accelerating voltage of 120 keV to investigate the dispersion and metal particle size of the catalysts. X-ray diffraction (XRD) with Cu K α radiation source (Philips PW-1840) was applied to study the crystalline phases of the catalysts and to obtain the average crystallite size of the nanoparticles (by Scherrer's equation). The green oil/oligomers resulting from the aged catalysts and the ones condensed in the outlet stream of the reactor were analyzed using Simulation Distillation analysis (SIM DIS, Varian Simulated Distillation 5.5), after dissolving in carbon disulfide. A Micromeritics TPD-TPR 2900 system was used to study the reduction behavior of tin-promoted and un-promoted Pd catalysts. A Micromeritics TPR/TPD was applied to investigate the amounts of hydrogen consumed for complete reduction of the catalyst. To perform TPR experiments, 40 mL/min 5% H₂/Ar was flowed through the cell, as the temperature was increased from the ambient temperature to 850 °C at a ramp rate of 10 °C/min.

The elemental analysis of metal content was obtained by a XL-30 energy dispersive X-ray (Philips). To find out the behavior of the aged catalysts, temperature programmed oxidation using an Agilent apparatus offline was applied. The sample aged for 36 h upon high concentrated acetylene hydrogenation reaction was exposed to a gaseous mixture of 5 vol.% air and 95% helium with a flow rate of 50 cm³/min, and then, heated from ambient temperature up to ca. 650 °C (5 °C/min). It is mentioned that catalysts examined were already gasified by argon, in order to remove less strengthened adsorbed species. X-ray photoelectron spectroscopy (XR3E2, 8025-BesTec) was applied to investigate the chemical states and the relative ratio of the elements on the surface of the catalyst. FTIR (Bruker, Vertex 70) was utilized to indicate the chemical nature of carbonaceous species formed upon aging the catalyst.

3. Results and discussion

TEM images of MWNTs-supported Pd nanocatalysts un-promoted and Sn-promoted are presented in Fig. 1. Comparison of the images 1a, b and c indicates a significant change in nanoparticle size with addition of tin. A distinct decrease of nanoparticle sizes is implied after addition of Sn to Pd molar ratio of 0.25 in comparison with the un-promoted Pd catalyst. According to the following photographs, one may observe that the Pd nanoparticles could have undergone a drastic depletion in nanoparticle size and also, a narrower particle size distribution with addition of tin. The un-promoted Pd nanoparticles sizes are found to be in the range of 6–10 nm; however, it decreases to an amount of 2.3–2.7 nm after addition of 0.25 M ratio of Sn to Pd. However, further addition of Sn promoter results in a slight increase in alloyed nanoparticle sizes, showing the size of 3–5 nm.

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