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Gold on carbon and titanium oxides composites: Highly efficient and stable acetylene hydrogenation in large excess of ethylene

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ABSTRACT

Photocatalytically generated gold on carbon and TiO_2 composites were used for acetylene hydrogenation in excess ethylene, in a way close to current industrial practices. The crystalline effect of TiO_2 and the addition of Pd to supported Au catalysts on acetylene hydrogenation were investigated. Carbon and amorphous TiO_2 supported Au were highly active, selective, and stable and possessed the highest ethylene yield of 83% at 210 °C with a H_2/C_2H_2 ratio of 2/1 for selective hydrogenation of acetylene to ethylene. With further addition of Pd to the supported Au catalyst, ethylene yield reached a maximum value of 57% at 30 °C with a H_2/C_2H_2 ratio of 2/1. The enhanced performance originated from small neutral Au nanoparticles and the formation of bimetallic Au–Pd catalyst. This report opens up promising possibilities for the design of highly efficient heterogeneous supported gold catalysts.

1. Introduction

Ethylene originated from thermal and steam cracking contains small acetylene impurities, which act as a poison for ethylene polymerization. The selective hydrogenation of acetylene is one of the acknowledged powerful routes to remove small amount of acetylene in ethylene streams [1]. High acetylene conversion and high ethylene selectivity are required for a good catalyst and subsequent ethylene hydrogenation to ethane should be avoided, in order to obtain a satisfactory ethylene yield. For more efficient catalysts, three targets should be achieved: (i) a high ethylene selectivity together with a high acetylene conversion; (ii) comparable performance at low H_2/C_2H_2 ratio at low reaction temperature; and (iii) long-term stability. Supported Pd catalysts are currently extensively used to remove acetylene contaminant in ethylene feedstock, because of their high acetylene conversion at low H_2/C_2H_2 ratios at relatively low temperatures [2–10]. For example, Pd catalysts are both highly active and selective for acetylene hydrogenation, which is attributed to the formation of Ag-alloyed Pd single atoms or Pd–Zn–Pd compounds with Ag or Zn as promoters [8,9]. Modification of Pd/TiO_2 catalyst by adsorption of triphenylphosphine and phenyl sulfide can significantly improve ethylene selectivity for acetylene hydrogenation in the presence of ethylene and excess hydrogen. The selectivity is still maintained owing to the sulfur deposition on the catalyst surface after ligand decomposition [10]. Moreover, 94% ethylene selectivity and 100% acetylene conversion are achieved on Pd_4S supported on carbon nanofibers at 250 °C with no significant decline of selectivity over 24 h [11]. Although Pd catalysts are active and relatively selective, there is still room to develop highly efficient and stable catalysts at low H_2/C_2H_2 ratios at low reaction temperatures.

Recently, supported Au catalysts have drawn tremendous interest for their high ethylene selectivity, owing to the unique properties of gold in having a much greater adsorption capacity toward acetylene than olefin molecules [12,13]. For instance, supported Au catalysts show 100% ethylene selectivity at temperatures up to 300 °C, whereas the selectivity decreases above 300 °C due to the formation of ethane [14,15]. Over the past few decades, much effort has been made to develop Au catalysts using different preparation methods, supporting materials, and bimetallic nanoparticles for the improvement of activity and durability in selective hydrogenation of acetylene [15–19]. However, supported Au catalysts exhibit relatively high activity at high reaction temperatures (above 200 °C) at a high H_2/C_2H_2 ratio [14–16]. In addition, Au catalysts suffer from quick deactivation under the above-mentioned reaction conditions. For instance, at 210 °C and a H_2/C_2H_2 ratio of 7/1, the activity of Au/CeO_2 decreased more than 40% within 6 h

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[15]. In our previous work, we used a photocatalysis method to prepare Au/C–TiO_2 catalysts for selective hydrogenation reactions [20]. This kind of Au catalyst is not only active and selective but also stable for selective hydrogenation of acetylene in ethylene. However, detailed studies are still needed for the improvement of catalytic activity and stability at low H_2/C_2H_2 ratios at low reaction temperature. Research on the relationship between catalytic performance and the structure of catalysts is also of great importance.

In this work, we applied a photocatalytic approach to preparing Au/C–TiO_2 catalysts by changing TiO_2 (P25 or amorphous) and forming bimetallic (Au–Pd) nanoparticles with the aim of enhancing acetylene conversion and ethylene selectivity along with long-term stability. X-ray diffraction, transmission electron microscopy, electron microscopy–energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and DRIFTs measurements are employed to investigate the structure of the catalyst and to reveal the structure–performance relationship.

2. Experimental

2.1. Catalyst preparation

Au/C–TiO_2 catalyst with 5 wt.% Au, 10 wt.% TiO_2 (P25), and carbon blacks (SC159, Sid Richardson Carbon and Energy Company) was fabricated according to previous work by a photocatalytic process (Fig. S1) [20,21]. In a typical process, carbon blacks mixed with TiO_2 (10 wt.%) were dispersed in 50 mL of deionized water using an ultrasonic bath to obtain a uniform composition of the C–TiO_2 support for receiving metal particles. The dispersion was transferred to a 500 mL volumetric flask, to which 13.5 mL HCOOH and the required solution volume of gold ($AuCl_4^-$) to generate Au (5 wt.%) were added. The total volume was then adjusted to 500 mL. The solution was poured into a UV photoreactor and maintained under constant N_2 bubbling to enhance particle dispersion in the solution. To study the effect of TiO_2 addition, an amorphous TiO_2 and carbon blacks-supported Au catalyst (5 wt.% Au, 10 wt.% amorphous TiO_2, and carbon blacks) was prepared according to the same procedure. Amorphous TiO_2 on carbon was prepared by weighing the required amount of titanium isopropoxide (Aldrich) and dissolving it in 200 ml of ethyl alcohol (Sigma-Aldrich). This solution was then mixed well with carbon and dried in a vacuum oven at 150 °C for 24 h. The C–TiO_2 composite powder was heat-treated in a regular oven at 400 °C for 1 h. To investigate the effect of Pd ($PdCl_4^{2-}$) addition, supported Au–Pd catalyst was obtained. Specifically, the procedure for preparation of Au–Pd/C–TiO_2 was similar to that of Au/C–TiO_2, except that it included sequential addition of Pd (5 wt.%) and then Au (5 wt.%) by a photodeposition method (Pd for 15 min and then Au for 15 min). Supported Au catalysts were denoted as Au/C–TiO_2-χ, where χ refers to crystalline (-P25) and amorphous (-am) TiO_2, respectively. After photodeposition was completed, the resultant catalyst was filtered and dried overnight at 70 °C. The dried powder was then finely ground. This photocatalysis approach contains reduction and oxidation processes (Fig. S2) [21]. In the reduction process, photogenerated electrons in TiO_2 were rapidly transferred by the carbon phase and delocalized on the entire C–TiO_2 surface. These electrons reduced the Au or Pd precursor to the metallic form. In the oxidation process, HCOOH was oxidized to CO_2 and acted as a hole scavenger in TiO_2.

2.2. Catalytic performance

All catalysts in powder forms were tested for the selective hydrogenation of acetylene in the presence of a large excess of ethylene. A 1/4 in. quartz reactor (i.d. 4 mm) housed in a GC oven with temperature-programmed heating and cooling capabilities was used in low temperature ranges. Catalysts (30 mg) were reduced in UHP hydrogen (Matheson, 99.999%) at 250 °C for 1 h and then underwent purging with UHP nitrogen (Matheson, 99.999%) at the starting reaction temperature before switching to the reaction mixture. The reaction temperature was kept constant for 30 min before being increased to the next temperature. Gaseous reactants were a mixture of 1.14% C_2H_2 in C_2H_4 with about 200 ppm C_2H_6 impurity (Scott Specialty Gases) and UHP H_2 to obtain different H_2/C_2H_2 ratios (2, 5, 10). Gaseous reactants were fed into the reactor at a space velocity of 92,000 mL h^{-1} g^{-1}. All flows were controlled by mass flow controllers. The analysis of the gas components from the microreactor was performed by an online Shimadzu GC 17A equipped with a 30 m × 0.32 mm (i.d.) × 1.50 μm GS-CARBONPLOT capillary column operating at 80 °C with a FID detector.

There was no signal of other hydrocarbon products detected by GC/FID except C_2H_4 and C_2H_6. Owing to the extremely high concentration of ethylene and small concentration of acetylene in the feed gas, if the calculation of ethylene selectivity is based on the difference of ethylene concentrations before and after the reaction, the error will undoubtedly be high. Therefore, the calculation of ethylene selectivity is based on the production of ethane from the reaction, assuming ethylene and ethane are the only products for acetylene hydrogenation. The calculations of acetylene conversion and the selectivity to ethylene and ethylene yield are as follows [7,8,16,19,20]:

$$\text{Conversion }(C_2H_2)\% = \frac{C_2H_2(\text{inlet}) - C_2H_2(\text{outlet})}{C_2H_2(\text{inlet})} \times 100\%,$$

$$\text{Selectivity }(C_2H_4)\% = \left[1 - \frac{C_2H_6(\text{outlet}) - C_2H_6(\text{inlet})}{C_2H_2(\text{inlet}) - C_2H_2(\text{outlet})}\right] \times 100\%,$$

$$\text{Yield }(C_2H_4)\% = \text{Conversion }(C_2H_2)\% \times \text{Selectivity }(C_2H_4)\%.$$

Given the fact that the conventional definition of the selectivity caused a large calculation error, we used “converted C_2H_2 - produced C_2H_6” to give the overall C_2H_4 selectivity, including the gain of ethylene from acetylene and the loss of ethylene in the feed. Because of overhydrogenation to ethane in the large excess of ethylene ($C_2H_4/C_2H_2 \sim 100$), the selectivity as defined in this work could be negative.

2.3. Catalyst characterizations

X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku D/Max-2500 diffractometer at a scanning speed of 4°/min over the 2θ range 10–90°. The diffractometer was equipped with a Ni-filtered CuKα radiation source (λ = 1.54056 Å). The phase identification was made by comparison to the Joint Committee on Powder Diffraction Standards (JCPDSs). The average size of the gold cluster was calculated with the Scherrer equation based on Au (111), Au (200), Au (220), Au (311), and Au (222) peaks.

Transmission electron microscopy (TEM) analyses were performed on a Philips Tecnai G2 F20 system operated at 200 kV. Scanning transmission electron microscopy–energy-dispersive X-ray spectroscopy (STEM-EDX) was also conducted using the same equipment combined with a Sirion200 field emission scanning electron microscope. The samples were finely ground, suspended in ethanol, and dispersed on a holey carbon-coated Cu grid.

X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD) was used to determine the Au4*f* and Pd3*d* binding energies of surface species with AlKα radiation. The correction of the binding energy employed the C1*s* peak of adventitious C at 284.6 eV. The spectra