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Enhancement of Pt catalytic activity in the hydrogenation of aldehydes

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ABSTRACT

Bifunctional mesoporous organic–inorganic hybrid silica involving platinum and propylsulfonic acid groups (Pt/SBA15-PrSO$_3$H) have been demonstrated to have potential for catalyzing the combined one-step hydrogenation/esterification (OHE) reaction. This reaction provides a model system for the catalytic upgrading of biomass-derived bio-oil. In this study, efforts were made to improve the catalytic performance of the catalyst for aldehyde hydrogenation, which was determined to be rate limiting in the OHE reaction with the bifunctional catalyst. STEM analysis coupled with hydrogen chemisorption results showed that aqueous reduction–deposition using formaldehyde as the reducing agent produced highly dispersed platinum nanoparticles located within the mesopores of SBA15. XPS and UV–vis demonstrated that the metal sites were not fully activated due to insufficient reducing capability of the formaldehyde. Elevated temperature treatment of the as-prepared materials in either an air or H$_2$ environment was examined. These treatments significantly increased the acetaldehyde hydrogenation activity, especially in the case of H$_2$ treatment. XPS and H$_2$-TPD results demonstrated that Pt species were further reduced and as a result, hydrogen was activated more readily.

1. Introduction

Bio-oil is a promising energy alternative for fossil fuels [1], but its corrosive nature due to a high content of organic acids and its reactive nature due to the presence of unsaturated components such as aldehydes necessitate upgrading for subsequent use [2]. The use of a combined one-step hydrogenation/esterification (OHE) reaction system has been explored as a possible approach for bio-oil upgrading by stabilizing the two main reactive components, aldehydes and organic acids, simultaneously [3]. Our previous work [3,4] indicated that the hydrogenation reaction is the rate-determining step for the OHE reaction system, so improvement of hydrogenation performance is vital for enhancing the overall OHE activity. Therefore, we have further focused on approaches to enhance hydrogenation activity of the bifunctional catalyst, which involved modifying the supported noble metal functionality of the catalysts.

Many strategies for preparing well-dispersed supported noble metal catalysts (e.g., Pt, Pd, Ir, etc.) have emerged and been investigated extensively during the last few decades, such as impregnation, precipitation, reduction–deposition, adsorption/ion-exchange, etc., which have resulted in the synthesis of catalysts having high catalytic activities when applied in a range of catalytic reactions [5,6]. It is believed that the catalytic performance of these supported metal catalysts depends on many factors such as morphology, dispersion and the electronic properties of the active metal sites [6].

Using the traditional impregnation method, severe conditions are usually needed to eliminate the accompanying components of the noble metal precursors [7,8]. For example, chloride removal from use of a metal chloride requires post-impregnation calcination at a temperature of at least 500 °C [8]. Unfortunately, such severe calcination conditions can lead to sintering, which is detrimental for highly dispersed metal sites [9]. Therefore, loading metals using an approach that utilizes milder conditions such as the aqueous reduction–deposition method was deemed promising to gain catalysts with highly dispersed metal sites.

In addition to anion removal, platinum incorporation using the various approaches is typically followed by an elevated temperature treatment to further activate the supported metal sites. This treatment requires further heating beyond drying and is carried out in different atmospheres (air, N$_2$, H$_2$, vacuum, etc.). Depending on the activation conditions, various (positive or negative) effects on catalytic performance are realized in different catalyst systems, such as removing chemically bonded H$_2$O or CO$_2$, modifying the nature of the phases present, generating the active phase, stabilizing mechanical properties, textural sintering that results in the loss of surface area and pore volume, and strong metal–support interaction (SMSI) [10–13]. Treatments under either reductive (H$_2$) or oxidative (air) atmospheres have been reported which have each led to favorable results [14–16]. Although it is most common for

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researchers to apply H_2 treatment to activate metal sites [14], Lamber and Romanowski [15] tested air treatment for Pt supported on silica and observed that Pt could be redispersed towards smaller particles compared with samples that were subjected to H_2 treatment. They ascribed this response to the splitting of Pt crystallites due to strain generated in the particles in the oxidative atmosphere. Additionally, it is possible for some supported noble metals that are present as oxides to undergo autoreduction during air treatment (in the atmosphere without any reductive agent) due to the thermal decomposition of the metal oxide [7,16].

High temperature treatments have been applied for platinum catalysts on many types of supports, such as TiO_2, SiO_2, Al_2O_3, La_2O_3 and ZrO_2 [17–21]. While careful control of the high temperature treatments can help to improve catalyst properties by maintaining high dispersions of the active metal phases on the supports due to suppression of metal migration and aggregation [20,22], it has also been found that high temperature pretreatment can induce sintering of Pt particles on Pt/Al_2O_3 [23]. With respect to the effects of thermal treatment on catalytic performance, improvements have been reported in numerous studies, such as the activity increase for acetylene selective hydrogenation on $Pd\text{-}Ti/SiO_2$ and the increase of methane production from CO and H_2 on Pt/TiO_2, etc., [24,25]. However, high temperature treatment in some cases can also inhibit catalytic activity, such as reported for naphthalene hydrogenation activity with $Pt/TiO_2–ZrO_2$ (1:1) [26] and CO photo-oxidation activity with $Pt/TiO_2(1\,1\,0)$ [27]. Therefore, whether high temperature treatment is favorable for catalyst properties and their catalytic performance will depend on the specific catalyst system being used.

The focus of the current work was activity enhancement for Pt supported on mesoporous silica. Aqueous reduction–deposition was employed to deposit Pt on the silica support rather than the traditional impregnation method and high temperature treatments were then applied after depositing the Pt. Air treatment and H_2 treatment at different temperatures were tested. Regarding the bifunctional catalyst $Pt/SBA15\text{-}PrSO_3H$ utilized in OHE reaction, because the organosulfonic acid groups cannot withstand high temperature treatment, they should be postgrafted to avoid the possible damage effect when treating Pt at high temperature. Consequently, it is different from previous work in that we are instead concerned about the procedures of loading Pt first. Therefore, monofuctional Pt/SBA15 was the focus in this work and the aim was to investigate the effect of different treatments so as to optimize the conditions for improving catalytic hydrogenation performance thereby providing guidance for further enhancement of the bifunctional catalysts (SBA15 functionalized with platinum and sulfonic acid group) to be used in the one-step hydrogenation/esterification reaction in the future.

2. Experimental

2.1. Catalyst preparation

The catalyst system examined in this work was only the monofuctional Pt/SBA15 material with the SBA15 support synthesized as described previously [4,28–30] with some modifications. Tetraethoxysilane (TEOS, 98%, Aldrich) was used as the silica precursor and Pluronic P123 (BASF), a triblock copolymer of polyethylene oxide–polypropylene oxide–polyethylene oxide with the molecular structure PEO20-PPO70-PEO20 (Mw = 5800), was used as purchased to tailor the textural properties of the mesoporous materials. An aqueous solution of platinum (IV) chloride ($PtCl_4$, Acros, 0.01 g Pt/ml) was used as the platinum precursor. Formaldehyde (HCHO, 37% by weight, aqueous solution, Fisher Scientific) was used as the reducing agent.

The nominal weight percentage of platinum on the catalysts was fixed at 1%. The nomenclature for the catalysts was assigned according to the preparation procedure used. The classification nomenclature used was the following abbreviations: "I" represents "incipient wetness impregnation"; "R_F" represents aqueous reduction–deposition by formaldehyde"; "C350″ stands for air treatment at 350 °C and "H350" stands for H_2 treatment at 350 °C. For example, the synthesis of the Pt/SBA15(I,C500) catalyst started with impregnating SBA15 in an aqueous $PtCl_4$ solution under a vacuum atmosphere (the solution volume was equal to the pore volume of SBA15) for 24 h. After drying at 110 °C overnight, the material received air treatment at 500 °C.

For the Pt/SBA15(R_F) series of catalysts, the first synthesis step was the dropwise addition of the formaldehyde solution at 60 °C into an aqueous suspension of SBA15 and $PtCl_4$ with vigorous stirring (1 g SBA15 with the corresponding amount of Pt in 30 ml of de-ionized water). The suspension was stirred for 24 h at 60 °C until its color changed from yellow to black indicating that the Pt was reduced to Pt^0, followed by filtering and drying. For those catalysts, which further received high temperature treatment, the air treatment step was performed at 200, 350, or 500 °C for 4 h, or the H_2 treatment was performed in flowing H_2 (300 ml/min) at 200, 350, 500 °C for 4 h.

2.2. Catalyst characterization

The textural properties of the catalytic materials were measured using the nitrogen adsorption–desorption method. The analysis was carried out at −196 °C using a Micromeritics ASAP 2020 system. The surface area, pore volume (V_p) and pore size distribution were calculated by the BET and BJH methods, respectively. The median pore diameter (MPD) of the samples was determined by the BJH method using the adsorption branch of the N_2 adsorption–desorption isotherm. All of the samples were degassed at 100 °C for 5 h before measurement.

The scanning transmission electron microscopy (STEM) images of the catalyst samples were obtained on a JEOL 2010F, 200 kV microscope. The X-ray photoelectron spectroscopy (XPS) experiments were carried out in a multitechnique chamber (Perkin–Elmer Model 5500) using PHI-ACCESS software for the analysis. The base pressure of the chamber was 3×10^{-10} Torr or less. The X-ray source provided monochromatized Al Kα radiation (1486.6 eV) at a power of 250 W. Binding energies were corrected for charge effects by reference to the C 1s peak at 284.6 eV.

The temperature-programmed desorption of H_2 (H_2-TPD) was carried out using a Micromeritics Autochem 2920 II system. The catalyst samples (0.100 g) were dried in Ar at 110 °C for 30 min and exposed to hydrogen flow for 30 min at room temperature and then flushed with flowing Ar for 60 min. The TPD experiments were performed using Ar as the carrier gas at a flow rate of 50 ml/min and a heating rate of 10 °C/min up to 700 °C.

The dispersion of platinum (D_{Pt}) on the surface of the support was determined by H_2 chemisorption performed on a Micromeritics ASAP 2020 C system. Samples were dried at 110 °C in vacuum followed by cooling to room temperature. Next, the samples were re-reduced in flowing hydrogen at 300 °C for 60 min (heating ramp 5 °C/min). Afterwards, the first isotherm was obtained using 50–400 mmHg of H_2 to determine the total adsorption. After the first total isotherm, the tube was evacuated under vacuum for 30 min to remove any reversibly adsorbed hydrogen. Then a second isotherm was performed at the same condition as the first isotherm. This second isotherm would yield the reversible adsorption, since at the start of this adsorption, all of the irreversible sites were covered. Finally, the difference of total-reversible was used to determine the irreversible isotherm profile (first isotherm–second isotherm).