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Comparison of impregnation and deposition precipitation for the synthesis of hydrothermally stable niobia/carbon

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ABSTRACT

In this study, nanostructured niobia particles supported on carbon supports (carbon black and carbon nanotubes) were prepared by two strategies: impregnation and deposition precipitation (DP). We compared the hydrothermal stability of these solid acid catalysts in the aqueous phase. At 15 bar and 200 °C, large niobia particles were formed due to crystallization on niobia/carbon composites prepared by impregnation (Nb/CB-I and Nb/CNT-I). In contrast, no large particles were formed on niobia/carbon composites prepared by DP (Nb/CB-DP and Nb/CNT-DP). For the aqueous phase dehydration of 2-butanol at 52 bar and 240 °C, deactivation was observed on the Nb/CB-I catalyst due to the formation of large niobia particles. The niobia/carbon catalyst prepared by DP (Nb/CB-DP) exhibited high catalytic activity, which was stable for over 40 h. The conversion of γ-valerolactone to pentanoic acid in the aqueous phase was carried out at 35 bar and 300 °C to investigate the stability of Pd nanoparticles on Pd/Nb/carbon bifunctional catalysts. The Pd nanoparticles were hydrothermally stable on the niobia/carbon composite prepared by DP, whereas the Pd nanoparticles sintered and were encapsulated by the niobia on the Pd/Nb_2O_5/CB-I. We conclude that the niobia/carbon composites prepared by DP method are much more hydrothermally stable due to the formation of nanosized niobia particles and a strong interaction between niobia and carbon. We present a roadmap for retaining oxide functionality and acidic properties under aqueous phase conditions which will be useful for future work in biomass-related aqueous reactions.

1. Introduction

Niobic acid ($Nb_2O_5 \cdot nH_2O$) is a solid acid catalyst that has been used extensively in important biomass reactions, such as dehydration, aldol condensation, hydrolysis and ketonization [1–4]. Niobium oxide is composed of distorted NbO_6 octahedra and NbO_4 tetrahedra and can provide both Lewis and Brönsted acid sites [1,3]. Recently, mesoporous niobium oxide with high surface area has been synthesized by self-assembly and antisolvent precipitation routes [5,6]. These mesoporous niobium oxides have been used successfully in both gas-phase and liquid-phase reactions at temperatures <150 °C, such as the dehydration of glucose to 5-(hydroxymethyl)furfural, Friedel–Crafts alkylation and esterification [3,6,7]. However, these pure amorphous niobium oxides were found to crystallize and lose surface area quickly in liquid water when used at temperatures greater than 200 °C, which resulted in deactivation of the catalyst [8]. We recently reported a new approach that we called deposition precipitation–carbonization (DPC) which provides improved hydrothermal stability due to a strong interaction between niobia and carbon [9]. However, the most common method to prepare supported catalysts is impregnation. For example, niobia/Al_2O_3 and niobia/MCM-41 composites have been recently prepared by impregnation [1,2], and found to exhibit good thermal stability upon heating to 850 °C [1]. However, when oxide supports are used under hydrothermal conditions, for example in the aqueous phase at temperatures of ≥200 °C, there is a loss of surface area and phase transformation leading to deactivation [10–13]. Carbon is a stable support under hydrothermal conditions, but it does not provide acid sites without additional pretreatment [14]. In order to provide acid sites in catalysts suitable for aqueous-phase reactions, we report here the synthesis of niobia/carbon composites.

In this study, two different methods (impregnation and homogeneous deposition precipitation) were used for depositing niobia on carbon. Deposition–precipitation (DP) has been developed by Geus et al. to prepare supported catalysts [15]. The use of urea ($CO–(NH_2)_2$) rather than that of sodium hydroxide allows solution mixing and precipitation to be performed in two separate steps: urea is mixed in the solution at room temperature, and urea hydrolysis starts when the mixture is heated to 90 °C; hydroxide ions are homogeneously generated within the solution, and precipitation only takes place onto the support because of the interaction

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between the metal ion species and the support. One of the advantages of deposition precipitation is that particles are smaller and the size distribution is narrower than catalysts prepared by impregnation [16,17]. Moreover, it is possible to deposit high metal loading ($\geq$20 wt%) as compared to catalysts prepared by cation exchange, which also leads to small metal particles [17,18]. In addition, the DP preparation method is highly reproducible [16]. More importantly, the dispersed nanoparticles prepared by DP method do not easily sinter because of their strong interaction with the support [19–22].

The niobia nanoparticles were supported on two different carbon supports (carbon black and carbon nanotubes). Due to its low cost and availability, we used carbon black (Vulcan XC-72) which has been extensively used as catalyst support in fuel cell catalysts [23–25]. Another novel carbon nanostructured material, carbon nanotubes (CNTs), has attracted attention recently for use as a catalyst support [26]. CNTs are composed of parallel graphene layers with a central pore and represent an interesting alternative to conventional supports for reasons that include their impressive mechanical properties, the high accessibility of the active phase and the absence of micro-porosity, thus eliminating intraparticle mass transfer in the reaction medium. Recently, two publications have reported that CNTs are stable in aqueous phase conditions and in supercritical water (SCW) [27,28].

In our work, the hydrothermal stability and catalytic activity of the niobia/carbon catalysts was systematically compared in three environments of increasing severity: (1) treatment in liquid water at 15 bar and 200 °C for 12 h to study the changes in the morphology; (2) aqueous phase dehydration of 2-butanol at 52 bar and 240 °C to study the catalytic stability of the niobia phase; and (3) The conversion of γ-valerolactone (GVL) to pentanoic acid at 35 bar and 300 °C, which requires acid sites for the ring-opening of GVL and metal sites for the hydrogenation of the reaction intermediate pentenoic acid to pentanoic acid. This model reaction allowed us to investigate the effect of the niobia/carbon support on the hydrothermal stability of Pd nanoparticles in these Pd/niobia/carbon bifunctional catalysts.

2. Experimental

2.1. Niobia/carbon catalyst preparation

2.1.1. Niobia catalysts supported on carbon black (CB)

Commercially-available carbon black (CABOT, Vulcan XC 72R) was firstly pretreated in 50% HNO_3 at 85 °C for 8 h, followed by filtration and washing with water till pH = 7. This treatment is necessary to oxidize the carbon surface and generate functional groups which make the carbon hydrophilic. The pretreated carbon was dried in air at 120 °C for 12 h. For the niobia/carbon catalyst with nominal niobium loading of 10 wt% prepared by a homogeneous deposition precipitation method (Nb/CB-DP), urea was used as the precipitating agent and the detailed synthesis route was as follows: ammonium niobium oxalate (0.41 g) and urea (0.27 g; 2.5 mol urea per mole of niobium) were dissolved in deionized water (250 mL) and added to 1 g of the functionalized carbon black (CB). Subsequently, the temperature was raised to 90 °C. After allowing sufficient time (17 h) for the hydrolysis of the urea, the sample was filtered and washed with deionized water, followed by drying at 100 °C for 10 h. The sample was denoted as Nb/CB-DP (DP stands for deposition precipitation).

For comparison, a niobia/carbon black catalyst with nominal niobium loading of 10 wt% was prepared by incipient wetness impregnation. The amount of liquid to fill the pores of the carbon was first determined. The appropriate amount of ammonium niobium oxalate solution was dissolved in deionized water and deposited dropwise onto the functionalized carbon black directly. Then, the sample was dried in air at 100 °C for 10 h. The material was calcined in a flow of N_2 at 280 °C for 6 h. The catalyst supported on carbon black prepared by impregnation was denoted as Nb/CB-I (I stands for impregnation).

2.1.2. Niobia catalyst supported on carbon nanotubes

Carbon nanotubes (CNTs) were prepared by chemical vapor deposition using a 5%Co/5%Fe/$CaCO_3$ catalyst as described in a previous study [29]. Briefly, the catalyst (0.5 g) was spread to form a thin layer in a ceramic boat and the boat was then placed in the center of a quartz tube. The furnace was heated at 10 °C min^{-1} under a flow of N_2 (40 mL min^{-1}). Once the temperature had reached 700 °C, the N_2 flow rate was set to 240 mL min^{-1} and C_2H_4 was introduced at a flow rate of 90 mL min^{-1}. After 60 min reaction, the C_2H_4 flow was stopped and the furnace was left to cool down to room temperature under a flow of N_2 (40 mL min^{-1}). The obtained CNTs were purified and functionalized in 50%HNO_3 at 85 °C for 8 h. After filtering and drying, the niobia/CNTs catalyst (10 wt%) was prepared by homogeneous deposition precipitation. The preparation procedure is similar to that for Nb/CB-DP, as described above. This niobia/CNT prepared by DP is denoted as Nb/CNT-DP. In addition, a Nb/CNT-I catalyst was prepared by impregnating the appropriate amount of ammonium niobium oxalate solution (10 wt%) onto the functionalized CNTs directly. Finally, the two niobia/CNT catalysts were calcined at 280 °C for 6 h in a flow of N_2.

2.2. Pd/niobia/carbon bifunctional catalyst preparation

Pd catalysts consisting of Pd (1 wt%) supported on niobia/carbon composites (Nb/CB-I and Nb/CB-DP) were prepared by incipient wetness impregnation of an aqueous solution of $Pd(NO_3)_2{\cdot}xH_2O$ (Alfa Aesar). The catalyst was dried in air at 100 °C overnight, followed by calcination at 250 °C (1 °C min^{-1}) in flowing N_2 (100 cm^3 min^{-1}) for 2 h.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded with a Scintag Pad V diffractometer using Cu $K\alpha$ radiation and a Ni filter. The scan range was 20–90° with 0.02° steps. Scanning electron microscopy (SEM) was performed on a Hitachi S-5200, with a resolution of 0.5 nm at 30 kV and 1.7 nm at 1 kV. Scanning transmission electron microscopy (STEM) was carried out in a JEOL 2010F microscope in the HAADF (high angle annular dark field) mode. An electron probe, diameter of 0.2 nm, was scanned over the specimen, and electrons scattered at high angles were collected to form the images. The powders were deposited on holey carbon support films after being dispersed in ethanol. N_2 adsorption–desorption experiment was conducted using a Quantachrome Autosorb-1. Prior to the experiment, the sample was outgassed at 200 °C for 6 h. The surface area was obtained using BET model for adsorption data in a relative pressure ranged from 0.05 to 0.30. The total pore volumes were calculated from the amount of N_2 vapor adsorbed at a relative pressure of 0.99. Thermogravimetric analyses (TGA) was performed with a SDT Q600 TGA using nitrogen as the purge gas and a heating rate of 10 °C min^{-1}. The flow rate of purge gas was always 50 mL min^{-1}. The zeta potential measurement was carried out in a Zetasizer Nano series. Carbon materials were dispersed in deionized water at room temperature and the pH of the suspension was adjusted from 2.0 to 12.0 by adding 0.1 M hydrochloric acid (HCl) or 0.1 M sodium hydroxide solution (NaOH) solution. By measuring the zeta potential as a function of pH, the point of zero charge (PZC) was determined. Ammonia temperature-programmed desorption (NH_3-TPD) was performed with a Micromeritics AutoChem II 2920 by degassing the sample at 300 °C for 30 min in Ar. Samples were then cooled to 50 °C in Ar and exposed to 10%NH_3in