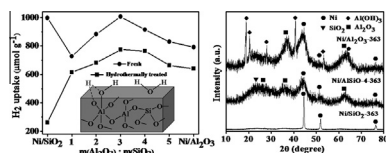# Preparation of highly active and hydrothermally stable nickel catalysts

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GRAPHICAL ABSTRACT

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ABSTRACT

The 60%Ni/AlSiO catalysts were prepared by the co-precipitation method, in which AlSiO were the composite supports with different mass ratios of Al_2O_3 and SiO_2. It was found that the catalyst 60%Ni/AlSiO-4 with the Al_2O_3/SiO_2 mass ratio of 4 in the support exhibited the high hydrothermal stability. The addition of proper amount of SiO_2 inhibited the hydration of Al_2O_3 and prevented the growth of supported nickel particles during the hydrothermal treatment. The structure of the composite support in the 60%Ni/AlSiO-4 was stable and the supported nickel particles were highly dispersed. Accordingly, the hydrothermally treated catalyst maintained the high heats and uptakes for the adsorption of H_2 and CO, and thus the high activity and stability for the hydrogenation of glucose to sorbitol in aqueous solution.

1. Introduction

The use of organic solvents in many industrial processes increases the costs and causes environment pollutions [1]. Water is cheap, safe and widely available and may be used as an environmentally benign solvent [2–4]. The hydrogenation reactions are widely applied in industry [5]. The hydrogenation reactions with the solvent of water have been developed and used in industries [6–8]. For instance, sorbitol is an important chemical widely used in food, cosmetic, paper and other fine chemical industries. Although it exists in a variety of fruits, the cost of extraction is high, so that its mass production is based on the hydrogenation of glucose in aqueous solution [9–11]. Crotyl alcohol is widely used in the fields of pesticide, paint and plasticizer, and it is usually produced by the hydrogenation of crotonaldehyde in organic solvents. Attention has been attracted to the hydrogenation of crotonaldehyde to crotyl alcohol in aqueous solution for the development of safer and greener process [12]. In addition, water would be generated in many hydrogenation reactions [13]. For example, the hydrogenation of nitrobenzene to aniline produces great amount of water [14]. Thus, the catalysts must withstand the severe hydrothermal environments for the hydrogenation reactions with water as a solvent or a product. The supports may be hydrolyzed, causing the collapse of pore structures and leading to the aggregation of supported active components and finally the deactivation of catalysts [15]. Thus, it is important to develop the highly active and hydrothermally stable catalysts. Unfortunately, the fundamental studies on such catalysts are rarely reported in open literature.

Nickel catalysts are active and cheap and supported nickel catalysts are widely used in hydrogenation reactions [16,17]. Alumina is a widely used support with high surface areas and thermal stabilities [18,19]. However, the hydrothermal stability of Ni/Al_2O_3 catalysts was poor, due to the easy hydration of Al_2O_3, leading to the significant decrease of surface areas and pore volumes and thus the aggregation of supported nickel particles and the loss

of catalytic activities [15]. In order to improve the hydrothermal stability of Ni/Al$_2$O$_3$ catalysts, it is necessary to improve the hydrothermal stability of the Al$_2$O$_3$ support. It is known that there are many unsaturated tetrahedral and octahedral voids in alumina [20], and the Al^{3+} cations in these voids are highly active and easily hydrated to form AlOOH, Al(OH)$_3$ or β-Al(OH)$_3$ species [21]. The occupation of these voids by some suitable additives could inhibit the hydration of Al^{3+} cations by water, improving the hydrothermal stability of alumina. Ravenelle et al. [22] prepared the Ni/γ-Al$_2$O$_3$ and Pt/γ-Al$_2$O$_3$ catalysts and studied the structural changes of these catalysts under hydrothermal conditions. They found that the presence of Ni and Pt particles significantly retarded the formation of boehmite. It has been reported that the Al–O–Al bonds in Al$_2$O$_3$ would be turned into Al–OH bonds in the hydrothermal environments. The addition of SiO$_2$ might lead to the formation of Si–O–Si and Si–O–Al bonds, eliminating the surface vacancies, leading to the increased hydrothermal stability of alumina [23]. Kang et al. [24] prepared the Ni/Al$_2$O$_3$–SiO$_2$ catalysts with different SiO$_2$ contents by the impregnation method and showed that the exposure of Al^{3+} could be reduced by the presence of SiO$_2$. The optimized content of SiO$_2$ was 3%, with which the Ni/ Al$_2$O$_3$–SiO$_2$ catalyst exhibited the best activity for the hydrogenation of 1,4-butynediol to 1,4-butanediol in aqueous solution.

Since the hydrogenation activity depends on the number of surface metal atoms, it is desirable to prepare the supported metal catalysts with the high loading, reducibility and dispersion [25]. The co-precipitation method was used in this work for the preparation of supported nickel catalysts with the high loading of Ni (about 60 wt.%). The composite metal oxides (termed as AlSiO-x) with different mass ratios of Al$_2$O$_3$ and SiO$_2$ (x) were used as the supports for the preparation of the Ni/AlSiO-x catalysts with the high hydrothermal stability. The techniques of H$_2$–O$_2$ titration, X-ray diffraction (XRD), transmission electron microscopy (TEM) and microcalorimetric adsorption were used to study the structures and surface properties of the fresh and hydrothermally treated catalysts. It was found that the catalyst Ni/AlSiO-4 exhibited the stable structure and the high active surface area and thus the high activity for the hydrogenation of glucose to sorbitol in aqueous solution.

2. Experimental

2.1. Preparation of catalysts

The catalysts Ni/Al$_2$O$_3$, Ni/SiO$_2$ and Ni/AlSiO-x (x = 1–5) containing about 60 wt.% Ni were prepared by the co-precipitation method. Specifically, the required amounts of Ni(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O were dissolved in 100 mL distilled water to form an aqueous solution (I). The required amounts of Na$_2$SiO$_3$·9H$_2$O and Na$_2$CO$_3$ were dissolved in 100 mL distilled water to form another solution (II). The two solutions were added simultaneously into a beaker containing 400 mL distilled water at 353 K under vigorous stirring. Green precipitates formed were filtered and washed thoroughly with distilled water until pH of the filtrate reached 7. Each of the filter cakes was dispersed into 200 mL n-butanol and heated at 353 K for 12 h to remove water and then n-butanol. The samples were further dried at 393 K in an oven overnight.

The hydrogenation of 1,4-butynediol to 1,4-butanediol was performed in aqueous solution in industry. The catalyst used for this process was the 17%Ni/Al$_2$O$_3$ prepared by the wet impregnation method [15]. In this work, a similar catalyst (17%Ni/Al$_2$O$_3$) was prepared for comparison by the incipient wetness impregnation method. The experimental results showed that the 60%Ni/AlSiO-4 was not superior over the 17%Ni/Al$_2$O$_3$ for the hydrogenation of 1,4-butynediol to 1,4-butanediol in aqueous solution. However,

the loading of nickel and thus the active Ni surface area were low in the 17%Ni/Al$_2$O$_3$, so that it might not be active for other hydrogenation reactions (for example, the hydrogenation of glucose to sorbitol) in aqueous solution.

The catalysts were reduced in flowing H$_2$ at 723 K for 2 h. After cooled down to room temperature, they were transferred under the protection of flowing H$_2$ into a 100 mL Teflon-lined stainless-steel autoclave containing 40 mL distilled water. After the autoclave was sealed, it was placed in an oven and heated for 8 h at 363, 393 and 423 K, respectively. The samples were then filtered and dried in an oven at 393 K for 12 h. The hydrothermal temperatures applied were added as the suffix to name the hydrothermally treated samples. For example, the catalyst Ni/ AlSiO-4 hydrothermally treated at 363 K for 8 h was termed as Ni/AlSiO-4-363.

2.2. Characterization of catalysts

The adsorption of H$_2$ and O$_2$ was carried out in a home-made volumetric apparatus. The catalyst was reduced in H$_2$ at 723 K for 2 h and evacuated at 723 K for 1 h before the measurements. The adsorption of H$_2$ was performed at room temperature. After the adsorption of H$_2$, the sample was heated to 673 K at a rate of 10 K/min and evacuated at the temperature for 1 h. The adsorption of O$_2$ was then performed at 673 K. The uptakes of H$_2$ and O$_2$ were obtained by extrapolating the coverage of corresponding isotherms to P = 0. The degree of reduction (reducibility), dispersion, average particle size and active surface area of supported nickel were calculated based on the amount of H$_2$ and O$_2$ adsorbed and the loading of nickel.

The chemical compositions of catalysts were measured by an ARL-9800 X-ray fluorescence spectrometer (XRF). XRD patterns were collected in ambient atmosphere by an X-ray diffractometer (Shimadzu XRD-6000) with Cu Kα radiation (λ = 1.5408 Å) generated at 40 kV and 30 mA. Diffraction intensities were recorded from 10° to 80° at a rate of 7°/min. TEM measurements were carried out using a JEOL electron microscope (JEM-2010) with an accelerating voltage of 200 keV.

The surface areas and pore sizes were measured by the Micromeritics Gemini V 2380 autosorption analyzer. Experiments were performed at 77.3 K using N$_2$ as an adsorbate. The samples were degassed in flowing nitrogen at 573 K for 3 h before the measurements. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were obtained by the Barrett–Joyner–Halenda (BJH) method according to the desorption branches.

Temperature-programmed reduction (TPR) measurements were performed by using a quartz U-tube reactor loaded with about 20 mg of a dried sample in 4.84% H$_2$/N$_2$ (v/v) at a flow rate of 60 mL/min. The temperature was raised from 303 to 1173 K with a programmed rate of 10 K/min.

Microcalorimetric measurements for the adsorption of H$_2$ and CO were performed using a Tian-Calvet type C-80 microcalorimeter (Setaram, France), connected to a glass vacuum system equipped with a Baratron capacitance manometer (USA) for the pressure measurements and gas handling. Prior to the microcalorimetric measurements, about 0.1–0.2 g of a catalyst were typically reduced in H$_2$ at 723 K for 2 h followed by the evacuation at the same temperature for 1 h.

The reduced catalysts were passivated overnight in N$_2$ containing about 1% O$_2$ before they were characterized by XRF, XRD, TEM and BET-BJH methods. The hydrothermally treated catalysts could be directly characterized by these techniques, but must be re-reduced in H$_2$ at 723 K before they were measured by the adsorptions and catalytic reactions.