Short Communication

Preparation and characterization of Ni-B/SiO$_2$sol amorphous catalyst and its catalytic activity for hydrogenation of nitrobenzene

Zili Liu [a,b,*], Yuna Li [a,b], Xuanyan Huang [b], Jianliang Zuo [a,b], Zuzeng Qin [c,**], Changwei Xu [a]

[a] School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, China
[b] Key Laboratory of Ministry of Education for Water Quality Security and Protection in Pearl River Delta, Guangzhou 510006, China
[c] School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

A B S T R A C T

Supported Ni-B/SiO$_2$sol amorphous alloy catalyst was prepared by a sol-gel and impregnation-chemical reduction method, and the effects of the tetraethyl orthosilicate (TEOS) and ammonia ratio, and the nickel loading amount on the nitrobenzene hydrogenation were also investigated. The results showed that Ni-B amorphous alloy catalyst supported on the silica sol increased the specific surface area of catalysts, improved the catalytic activity of Ni-B amorphous alloy catalyst, and the Ni species on the surface existed in the form of Ni^{2+}. The optimal TEOS and ammonia ratio and nickel loading amount was 1.0 and 10%, respectively, and when using this optimal Ni-B/SiO$_2$sol catalyst, the nitrobenzene conversion was 99.9% with an aniline selectivity of 99.8%, and after 5 recycles, the Ni-B/SiO$_2$sol maintained a good stability.

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1. Introduction

Catalytic hydrogenation of nitrobenzene is the dominant process for the industrial scale production of aniline [1], which serves as an important intermediate to producing polyurethanes, intermediates dyes, and pharmaceuticals [2–4]. As the increasing of the demand for aniline, the efficiency of this hydrogenation process become more and more important. About 85% of aniline is produced by catalytic hydrogenation of nitrobenzene, which can be performed in gas or liquid phase using supported metal catalysts and organic solvents such as alcohols, acetone, benzene, ethyl acetate, or aqueous acidic solutions [5,6], electrochemical synthesis and iron based reduction in acidic media [7]. Ni is an active catalyst for epoxidation [8] or hydrogenation [9,10], and Raney metals (such as Raney Ni [11], Raney Cu [12], etc.) and the supported noble metals [13,14] are the main catalysts for the hydrogenation of nitrobenzene, which has been researched and applied widely. However, the former had the problem of poor selectivity and environmental pollution, the latter were high cost, or in some cases, the active species was suffered severe leaching also another problem [15,16].

Recently, metal-metalloid amorphous alloy catalysts caused much attention due to their isotropic, unsaturated of its surface atoms coordinating, short-range order and long-range disorder by uniform chemical structure, and its high catalyltic performance, as well as their strong sulfur resistance in various hydrogenation reactions [2,17–23]. However, amorphous alloy catalysts have less specific surface area and poor thermal stability, which easily deactivate by forming crystal [23], and seriously affected their industrial application.

Therefore, maintaining the high catalytic activity and the thermal stability of amorphous alloy catalyst becomes a main target in the field. Based on the previous study of Ni-P amorphous alloy catalyst [2, 23], in the present work, Ni-B amorphous alloy was supported on SiO$_2$sol, characterized and applied in the liquid phase hydrogenation of nitrobenzene to aniline.

2. Experimental and methods

2.1. Catalysts preparation

Si(C$_2$H$_5$O)$_4$, CH$_3$CH$_2$OH, NH$_3$·H$_2$O, NiAc$_2$·6H$_2$O, KBH$_4$, and NaOH (Sinopharm Chemical Reagent Co., Ltd) are analytical grade and without any further purification before using. The silica sol was prepared by using a sol-gel method [24]: 0.05 mol tetraethyl orthosilicate (TEOS, Si(OC$_2$H$_5$)$_4$) was dissolved in ethanol at a Si(OC$_2$H$_5$)$_4$ and CH$_3$CH$_2$OH mole ratio of 1: 9, the ammonia was slowly added at a TEOS and ammonia mole ratio of 1: x(x = 0.2, 0.5, 1, 1.5, 2.0). After a 4-hour reaction, a 0.5 mol/L NiAc$_2$·6H$_2$O aqueous solution was added and reacted at room temperature for 12 h, and a Ni/silica sol was obtained. Subsequently, a 0.5 mol/L KBH$_4$ aqueous solution, which pH was adjusted by the 2 mol/L NaOH to 12, was dropwise added to the Ni/silica sol, and a

black precipitate was formed and was accompanied by the evolution of gas bubbles. When the bubbles were no longer generated in the solution, the reaction in mixture solution was stopped, and the precipitate was collected by filtration of the solution. The precipitate was washed with distilled water until the filtrate pH was 7, and the precipitate was then washed with ethanol several times to remove the water in the catalyst, and the Ni-B/SiO$_2$sol amorphous catalysts with different TEOS and ammonia ratio and nickel loading amount were obtained and stored in ethanol.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected on a D/MAX2500V X-ray powder diffraction (Rigaku, Japan). Scanning electron microscopy (SEM) images were taken on a JSM-7001F thermal field emission scanning electron microscope (JEOL Co., Ltd.). The oxidation state and surface composition were analyzed using an X-ray photoelectron spectrometer (XPS) (Kratos Ultra Axis DLD), equipped with an Al Kα radiation source, at 150 W with a pass energy of 40 eV. The isotherm of nitrogen adsorption and desorption was measured by an ASAP 2000 physical adsorption instrument (Micromeritics Instrument Corp.).

2.3. Nitrobenzene hydrogenation to aniline on Ni-B/SiO$_2$sol

Catalytic transformation of nitrobenzene was performed in a 50 mL stainless autoclave equipped with an electromagnetic driven stirrer. For a typical test, 0.1 g Ni-B/SiO$_2$sol amorphous catalyst, 1.0 g nitrobenzene, 4.0 g absolute ethyl alcohol were added into the autoclave. After purging the reactor with H$_2$ five times to exchange the air in the autoclave, the hydrogenation of nitrobenzene was conducted at 1.8 MPa and 100 °C for 120 min. Subsequently, the reactor was cooled to room temperature quickly and the liquid phase product mixture was separated from the catalyst by centrifugation. The products were analyzed by a 2014C gas chromatography (Shimadzu Corporation) using methylbenzene as an internal standard.

3. Results and discussion

3.1. XRD of Ni-B/SiO$_2$sol amorphous catalysts

The XRD patterns of Ni-B/SiO$_2$sol amorphous alloy catalysts prepared using different TEOS and ammonia ratio and the Ni loading amount were shown in Fig. 1 and Fig. S1 (Fig. S1 in the Appendix A.
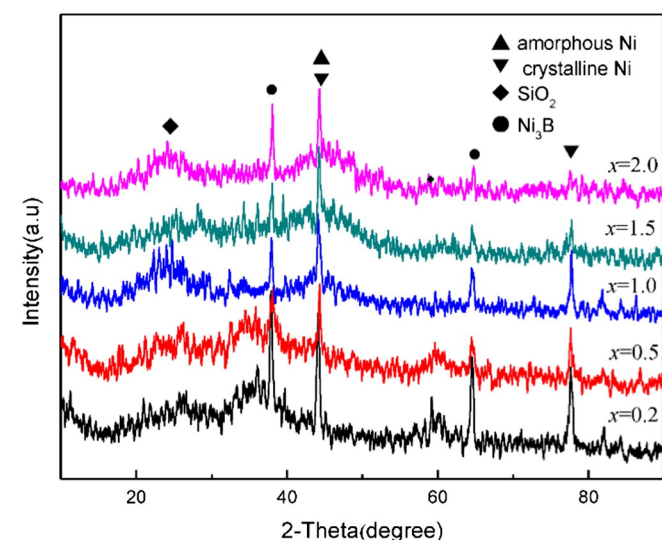

Fig. 1. XRD patterns of Ni-B/SiO$_2$sol amorphous alloy catalysts with TEOS and ammonia ratio from 0.2 to 2.0.

Supplementary data). In Fig. 1, when the TEOS and ammonia ratio was 1.0, there is a small peak around $2\theta = 22°$, corresponding to the amorphous SiO$_2$; and a broad diffraction peak around $2\theta = 45°$ was observed, indicating a typical amorphous structure [2,25–27], the diffraction peaks located at $2\theta = 38$, and 64° was the crystalline Ni$_3$B diffraction peak, and at $2\theta = 45$, and 78° was crystalline Ni diffraction peak. However, the small peak around $2\theta = 22°$ and the broad diffraction peak at around 45° could not be found when the TEOS and ammonia ration was lower than 1.0. When TEOS and ammonia ratio was higher than 1.0, a broad diffraction peak around $2\theta = 45°$ was found with a sharp diffraction peak of crystalline Ni, and the SiO$_2$sol peak at $2\theta = 22°$ exhibited similar tendencies, the peak intensity increased with the increasing of the TEOS and ammonia ratio from 1.0 to 2.0.

In Fig. S1, when the Ni loading amount was lower, i.e., 5% or 10%, the broad diffraction peaks around $2\theta = 45°$ couldn't be observed due to the less amorphous nickel amount, and the nickel diffraction on the surface of the support SiO$_2$sol evenly, which could not be detected by the diffractometer. With the increasing of the Ni loading amount, the intensity of the amorphous Ni peak, located at around 45°, was increased. And obvious changes of the intensity of diffraction peaks at $2\theta = 45°$, and 60°, and 78°, attributed to crystalline Ni, were also increased with the increasing of Ni loading amount. At the same time, the peak at about 25°, attributed to the support SiO$_2$sol, become weak with the increasing of the Ni loading amount, indicating the SiO$_2$sol structure may be destroyed.

3.2. SEM and EDS of Ni-B/SiO$_2$sol amorphous catalysts

SEM images of the Ni-B/SiO$_2$sol amorphous alloy catalysts prepared with 10% nickel loading amount and at a TEOS and ammonia ratio of 0.5, 1.0, and 2.0, and 40% nickel loading amount and at a TEOS and ammonia ratio of 1.0 show in Fig. S2. The four Ni-B/SiO$_2$sol amorphous alloy catalysts were spherical particles with a cotton-like morphology, the surface Ni-B adhered on the sphere surface at small clusters in uniform grid form uniformly [28]. Firstly, the effects of the TEOS and ammonia ratio on the catalyst morphology were shown in the Fig. S2(a), (b), and (c). When the TEOS and ammonia ratio was 0.5, the catalyst particle size was about 220 nm, Ni-B/SiO$_2$sol exhibited an amorphous form, and the Ni-B was intricately formed to the SiO$_2$sol support. When the TEOS and ammonia ratio was 1.0, the catalyst particle size was about 230 nm, Ni-B amorphous alloy uniformly supported on the SiO$_2$sol network structures with a good dispersion. When the TEOS and ammonia ratio was 2.0, the catalyst particle size was about 310 nm, Ni-B amorphous alloy aggregated on the SiO$_2$sol surface with a relatively lower dispersion. These results indicated the ammonia amount affected the particle size of the catalysts and the distribution of Ni-B amorphous alloy on the SiO$_2$sol support, and with the increasing of the TEOS and ammonia ratio from 0.5 to 2.0, the Ni-B/SiO$_2$sol particle size increased, and tends to a spherical particle with a particle size greater than the conventional silica particle size of 10–20 nm.

Secondly, the effects of the Ni loading amount on the catalyst morphology were shown in Fig. S2(b) and (d), the Ni-B/SiO$_2$sol amorphous alloy catalysts were both uniform spherical particles at a Ni loading amount of 10% and 40%. When the nickel loading amount was 40%, the catalyst particle size was about 220 nm, Ni-B amorphous alloy seriously aggregated on the SiO$_2$sol surface with a lower dispersion, and some of the Ni-B amorphous alloys separated from the SiO$_2$sol. The 10% nickel loading amount Ni-B/SiO$_2$sol catalysts exhibited a good Ni-B dispersion at a particle size of 230 nm, which may increase the catalytic activity of the Ni-B/SiO$_2$sol amorphous alloy catalyst in the hydrogenation of nitrobenzene to aniline, and the 10% was the optimal Ni loading amount in this study. From the results of energy dispersive spectroscopy (EDS), the Ni percentage of the Ni loading amount of 5%, 10%, 15%, 20%, 30%, and 40% was 0.16%, 0.41%, 0.52%, 1.57%, 2.23%, and 4.44%, respectively.

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