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Synthesis of Ru-B amorphous alloy supported on SBA-15 with excellent catalytic efficiency in maltose hydrogenation

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ABSTRACT

Mesoporous silica (SBA-15)-supported Ru-B catalyst was synthesized by ultrasound-assisted incipient wetness infiltration of $(NH_4)_2RuCl_6$ into SBA-15 and a subsequent reduction with BH_4^-. It was characterized by X-ray diffraction, X-ray photoelectron spectroscopy, differential scanning calorimetry, and transmission electron microscopy. The resulting Ru-B-X/SBA-15 catalyst was identified to be an amorphous alloy highly dispersing within the pore channels of SBA-15. During liquid-phase maltose hydrogenation, the as-synthesized Ru-B-X/SBA-15 catalyst was more active than the Ru-B-C/SBA-15 obtained via the same process but using $RuCl_3$ as the metal source. The as-prepared Ru-B-X/SBA-15 delivered catalytic activity up to seven times greater than that associated with the reference unsupported Ru-B-C catalyst prepared through the reduction of $RuCl_3$ with BH_4, and could be used repetitively 11 times without significant deactivation.

1. Introduction

Hydrogenation of maltose to maltitol (Scheme 1) is of great importance because of the potential application of maltitol as a sugar substitute in modern nutrition, in diabetic food, and as an intermediate for pharmaceutical production [1]. Presently, Raney Ni is used in this industrial process [2]. However, the leaching of nickel during hydrogenation and the poor selectivity to maltitol make this catalyst less profitable. A refilling of the catalyst and a purification of product to remove residual Ni and other byproducts are necessary, which eventually increase the overall cost [3]. Amorphous alloys, metastable materials with long-range disordered but short-range ordered structure, have attracted growing attention from both academia and industry because of their superior catalytic properties to their crystalline counterparts [4,5]. Ru-based amorphous alloy has proved to be a potential alternative to Raney Ni in selective hydrogenations of benzene to cyclohexene [6], glucose to sorbitol [7], and maltose to maltitol [8]. Generally, Ru-B amorphous alloy was prepared by the reduction of Ru^{3+} with BH_4^- in aqueous solution [4]. However, vigorous and exothermic reactions between metallic ions and BH_4^- usually induce particle aggregation, thereby reducing catalytic activity. Recently, we have developed an approach to synthesizing monodispersed Ru-B amorphous alloy through ultrasound-assisted chemical reduction of $(NH_4)_2RuCl_6$ with BH_4^- in aqueous solution [9]. The coordination of halide ligands to Ru^{3+} resulted in the formation of ultrafine Ru-B amorphous alloy with high dispersion, which exhibited much higher catalytic activity relative to the Ru-B prepared by reduction of Ru^{3+} with BH_4^-. However, their industrial

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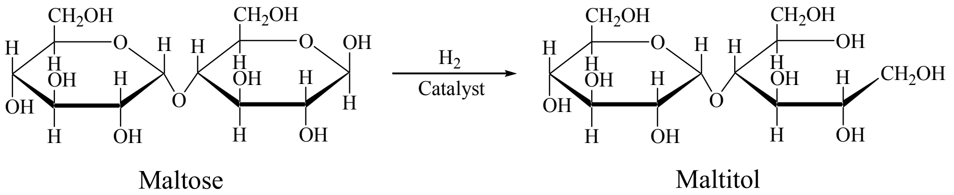

Scheme 1. Catalytic hydrogenation of maltose to maltitol.

application is still limited because of the high cost of Ru, as well as the low surface area and poor thermal stability of Ru-B amorphous alloy. The development of supported Ru-B amorphous alloy catalysts with improved thermal stability seems a promising option.

Because of high surface areas, ordered pore channel, and uniformity in pore size, highly ordered mesoporous materials can act as promising carriers for depositing amorphous alloy nanoparticles [10]. However, the supported amorphous alloy made with pure mesoporous silica usually exhibits non-uniform distribution and even blockage of the pore entrance, which eventually limits the activity. Although the metal dispersion can be improved through the modification of the surface of mesoporous silica (SBA-15) with hydrophobic functional groups [11], this approach involves a complicated preparation process. With the aim of designing powerful catalysts for maltose hydrogenation to maltitol, we report the synthesis of supported Ru-B amorphous alloy through ultrasound-assisted incipient wetness infiltration of $(NH_4)_2RuCl_6$ into SBA-15 and a subsequent reduction with BH_4. This product exhibited much higher activity and improved durability than the conventionally prepared Ru-B amorphous alloys during maltose hydrogenation. The correlation of the catalytic performances to the structural properties has been tentatively established.

2. Experimental

2.1. Catalyst preparation

SBA-15 silica was synthesized according to the method reported by Zhao et al. [12]. The supported Ru-B catalyst was prepared by the following procedure. SBA-15 (1.0 g) was impregnated with 8 ml of $(NH_4)_2RuCl_6$ aqueous solution (0.062 mol/L), which was sonicated for 2 h with an ultrasonic bath (60 W). After being calcined at 473 K for 2 h, 1.5 ml of KBH_4 aqueous solution (2.0 mol/L) was added dropwise at 273 K and was stirred continuously until no bubbles were released. The solid was washed free from Cl^- and K^+ ions with deionized water until a pH~7 was achieved. The as-prepared Ru-B sample was denoted as Ru-B-X/SBA-15, with X representing the metal source, $[RuCl_6]^{2-}$ complexes.

For comparison, the reference Ru-B catalysts were prepared through the conventional method. Unsupported Ru-B amorphous alloy was prepared by direct reduction of $RuCl_3$ with BH_4^-, which was denoted as Ru-B-C. Supported Ru-B amorphous alloy was prepared by the same process as described above for Ru-B-X/SBA-15, except that $RuCl_3$ was used as the metal source and was denoted as Ru-B-C/SBA-15. Raney Ni was commercially available and was used without further treatment.

2.2. Catalyst characterization

The bulk composition was analyzed by means of inductively coupled plasma optical emission (ICP, Varian VISTA-MPX). The amorphous structure was investigated by both X-ray diffraction (XRD, Rigaku D/Max-RB with Cu K_α radiation) and selected-area electronic diffraction (SAED, JEOL JEM-2100). The crystallization process was followed by differential scanning calorimetry (DSC, Shimadzu DSC-60) under an N_2 atmosphere at the heating rate of 10 K/min. The surface morphology and the particle size were observed by transmission electron microscopy (TEM, JEOL JEM-2100). The surface electronic states were investigated by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI5000 VersaProbe using Al K_α radiation), during which all Ru-B samples were dried and pretreated in situ in pure Ar atmosphere to avoid oxidation. The active surface area (A_{act}) was measured by hydrogen chemisorption on a Micromeritics AutoChem II 2920 system assuming H/Ru(s) = 1 and a surface area of 6.1×10^{-20} m^2 per Ru atom.

2.3. Activity test

The liquid-phase hydrogenation of maltose was performed at 3.0 MPa of H_2 pressure and 373 K in a 200-ml stainless steel autoclave with a Teflon tube to avoid metal contamination, in which Ru (0.05 g, 0.5 mmol) and a maltose aqueous solution (40% *w*/*w* in 50 ml H_2O) were well mixed. According to the drop of the H_2 pressure in the autoclave with reaction time, both the specific activity (the H_2 uptake rate per gram of Ru, R_H^m, mmol/(h·g)) and the intrinsic activity (the H_2 uptake rate per m^2 of Ru, R_H^S, mmol/(h·m^2)) were calculated using the ideal gas equation. After reaction for 0.5 h, the reaction products were analyzed in a liquid-phase chromatograph (Agilent 1100) equipped with a carbohydrate column (CARBOSep, Coregel-87C) and a refractive index detector at 353 K with water as the movable phase at 0.6 ml/min. Preliminary kinetic studies revealed the following: that there was a plateau in the dependency of the reaction initial rate when the stirring rate was above 1000 r/min; and that the reaction initial rate varied linearly with the catalyst amount from 0.1 to 2.0 g, indicating that the stirring rate of 1200 r/min was high enough that the hydrogenation rates were independent of mass transfer.

3. Results and discussion

3.1. Catalyst characterization