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Reduction of cobalt ion improved by lanthanum and zirconium as a triphenylphosphine stabilized nano catalyst for hydrolysis of sodium borohydride

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ABSTRACT

La–Zr co-doped Co–B nanoparticle stabilized by Triphenylphosphine (TPP) is for the first time prepared in situ reduction by sodium borohydride at reflux condition. Obtained powders were characterized by XRD, BET, ICP, SEM–EDS and TEM techniques. TEM images depict that Co–B is appears formless and agglomerated powder. There are no agglomerated TPP stabilized La–Zr co-doped Co–B nanoparticles. It is concluded that, TPP as stabilizing agent can prevent agglomeration. TPP stabilized nanoparticle is formed as a spherical shaped particle. Particle size distribution is prepared and average size particle is about 13 nm. TPP stabilized La–Zr co-doped Co–B nanoparticle is highly active catalyst for hydrogen generation through the hydrolysis of sodium borohydride. It is also includes the full experimental details for the collection of a wealth of kinetic data to determine the activation energy ($E_a = 45 \text{ kJ mol}^{-1}$). Catalytic hydrolysis of NaBH_4 is first order with respect to the catalyst concentration and also first order to the NaBH_4 concentration in the case of TPP stabilized La–Zr co-doped Co–B nanoparticles.

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Introduction

Metal nanoclusters have been used as catalysts in various reactions [1]. Metal nanoparticles often show very interesting physicochemical properties [2]. Activity of them depends on their size, morphology and surface composition [3,4]. NaBH_4 has been reported as a new fuel source for supplying hydrogen [5]. M–B (metal-boride) prepared by reducing metal salts with sodium borohydride was good catalysts for the hydrolysis reaction [6,7]. Hydrogen generation yield can be enhanced by using several precious metals Pt [8], Pd [9] and Ru [10]. In order to obtain stable nanoparticles dispersed in solution, a

stabilizing agent is usually added into the reaction system. In the literature of colloidal stability [10] colloidal stabilization is well established to involve: (i) electrostatic stabilization by the surface adsorbed anions such as chloride or citrate ions [11], (ii) polymeric stabilization such as polyvinylpyrrolidone (PVP) [12] and (iii) steric stabilization by the coordinating ligands such as triphenylphosphine (TPP) [13]. TPP is a high-boiling point surfactant with a patulous long-chain structure providing great steric hindrance. Previous papers proved that the alloy catalysts in the form of Co–W–B [14], Co–Mn–B [15], Ni–Co–B [16], Co–Cu–B [17] and Co–Ni–B [18] exhibit good catalytic activity as compared to Co–B. Previously, we have synthesized Co–La–Zr–B quaternary amorphous nano alloy

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and PVP stabilized crystalline phase of Co–La–Zr–B under ultrasound and reflux condition, respectively, for hydrogen generation through hydrolysis of sodium borohydride [19,20]. Our last reports confirmed that Lanthanum and Zirconium can avoid agglomeration of the Co–B particles. In addition, we reported ability of oleic acid as long chain fatty acid on size, morphology and catalytic activity of catalyst through hydrogen generation reaction [21]. In this work, TPP as stabilizing agent was used to formation of separated nano scale particles. It is tried to more separation of nano scale particles by addition of TPP. Obtained powders were characterized by XRD, BET, ICP, SEM-EDS and TEM techniques. Activity of bare La–Zr co-doped Co–B, TPP stabilized La–Zr co-doped Co–B and Co–B powders were tested for hydrogen generation through hydrolysis of sodium borohydride alkaline solution. In order to approach the rate law for hydrogen generation several parameters were studied.

Experimental

TPP stabilized La–Zr co-doped Co–B nanoparticles were prepared at Ar atmosphere. First, in 250 mL three-necked round bottom flask, 238 mg (1 mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 371 mg (1 mmol) of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 233 mg (1 mmol) of ZrCl_4 were dissolved in 50 ml methanol. Next 5 mmol of TPP (1311 mg), was added in metals solution. Color of solution is purple at this moment. Then, the mixture was refluxed for 1 h. Color of solution was gradually changed to blue. Immediately after reflux, 10 ml of sodium borohydride solution (9 mmol = 342 mg NaBH_4 in methanol) was added drop by drop into stabilized metals solution. By addition of NaBH_4 solution, abrupt color change from blue to black indicates that the formation of metal nanoparticles was completed. Methanol was removed from the solution by evaporation and powders were washed with hot methanol several times. Co–B is also synthesized by same method without Lanthanum, Zirconium salts and TPP. In addition, for show TPP effect on size, morphology, and hydrogen generation activity bare La–Zr co-doped Co–B is also synthesized without TPP as stabilizer agent.

Hydrogen generation

Investigation of hydrogen generation through hydrolysis of NaBH_4 was conducted in a batch system equipped with a thermometer. There is an outlet to collect the generated hydrogen gas. Hydrogen volume was measured by monitoring the water displacement from the inverted cylinder as the hydrolysis proceeded. It was not needed stirring during the reaction because releasing of hydrogen gas induced enough mixing effect. In order to investigation of kinetics data, three different sets of experiments were performed. In the first set of experiments, the concentration of NaBH_4 was kept constant at 5 wt%, and the TPP stabilized La–Zr co-doped Co–B dosage was varied of 6, 12, 25, 40 and 50 mg. In the second set of experiments, TPP stabilized La–Zr co-doped Co–B dosage was held constant at 50 mg while the NaBH_4 concentration was varied of 1.25, 2.5, 5, 7.5 and 10 wt%. The third set of experiments was performed by keeping NaBH_4 and TPP stabilized La–Zr co-doped Co–B concentrations constant at 5 wt% and

50 mg, respectively, and testing the temperature effect at 20, 25, 30, 35 and 40 °C. Although the self-hydrolysis of sodium borohydride at room temperature is quite slow, it can be completely suppressed by working in highly basic solution [22].

Characterization methods

X-ray diffraction patterns were recorded in D8 Bruker Advanced, X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\alpha = 1.54 \text{ \AA}$). Transmission electron microscope image was obtained in Philips CM10 transmission electron microscope with an accelerating voltage of 100 kV. The Cobalt, Lanthanum and Zirconium content of the samples were determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Leeman-Direct Reading Echelle). Specific surface areas of catalysts were measured by the BET method analysis under N_2 adsorptive (SIBATA SA 1100) after degassing.

Results and discussions

Characterization

XRD patterns of Co–B, bare La–Zr co-doped Co–B and TPP stabilized La–Zr co-doped Co–B powders are shown in Fig. 1. It can be seen that Co–B and TPP stabilized La–Zr co-doped Co–B powders are crystallized and there are one and four peaks in XRD patterns, respectively. In fact, it is a mixture of different Co–B compounds. Fig. 1 (a) shows XRD pattern of Co–B catalyst. The peak around $2\theta = 45$ is corresponded to metallic Cobalt and borides compounds [23]. Fig. 1 (b) and (c) are corresponded to bare La–Zr co-doped Co–B and TPP stabilized La–Zr co-doped Co–B powders, respectively. The peak around $2\theta = 32$ is corresponded to Zr and ZrB [24]. The diffraction peak around $2\theta = 45$ is overlapped by the peaks of CoB, CoB_2 and Co_2B compounds and metallic Cobalt. Next peak, $2\theta = 57$, is attributed to Zr and CoB. Low intense peak around $2\theta = 65$ is probably corresponded to ZrCo_3B_2 [25]. There is not seen any peak attributed to Lanthanum element. The standard reduction potentials of Co^{2+}/Co , La^{3+}/La and Zr^{4+}/Zr are -0.28 , -2.379 and -1.45 V relative to the standard hydrogen electrode, respectively. As seen, the standard reduction potential of La^{3+}/La is very negative. Therefore, La^{3+} ion cannot be reduced to La. It is not obvious any peak attributed to impurities. In addition, there is not any peak of Co_3O_4 , La_2O_3 , ZrO_2 and B_2O_3 in XRD pattern indicating formation of metal oxide is inhibited under Ar atmosphere. Determination of size and morphology of powder are accomplished by TEM micrograph. Fig. 2 shows TEM images of Co–B, bare La–Zr co-doped Co–B and TPP stabilized La–Zr co-doped Co–B powders. As seen in Fig. 2 (a), Co–B is appears formless and agglomerated powder. Fig. 2 (b) shows TEM micrograph of bare La–Zr co-doped Co–B powder. After addition of Lanthanum and Zirconium several particles with clear border are formed and agglomeration of powder is decreased. As clearly seen, Fig. 2 (c), there are no agglomerated TPP stabilized La–Zr co-doped Co–B nanoparticles. TPP as stabilizing agent can separate particles more than Lanthanum and Zirconium, Scheme 1. Indeed, TPP as a monodentate

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