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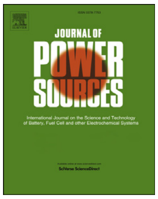

Short communication

Self-protective cobalt nanocatalyst for long-time recycle application on hydrogen generation by its free metal-ion conversion

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HIGHLIGHTS

- We have explored a facile but very efficient method to realize the long-time recycle application of Co nanocatalyst.
- Oxidizes Co^0 completely into Co^{2+} for the long-time and oxygen-fearless storage in air.
- Reduces Co^{2+} back to fresh and highly active Co^0 for the recycle application in air.
- There is no obvious decrease in activity after 20th recycle application (73 days) for hydrogen generation in air.

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ABSTRACT

Cobalt nanoparticles have attracted much attention in nanocatalysis due to their low cost and high activities. However, the easy-oxidative deactivation of cobalt nanocatalysts in air seriously limits their practical applications, especially in a long-time recycle application. Herein, by intentionally taking advantage of the readily oxidizable character of metallic cobalt, we describe a simple but efficient method to overcome the above obstacle through a free and reverse metal-ion conversion of cobalt in air at room temperature. With this novel method, the cobalt nanocatalyst demonstrates the superior activity even after the long-time (73 days) recycle application for hydrogen generation from ammonia borane.

1. Introduction

Nanocatalysis contributes significantly to many important chemical reactions due to the large surface-to-volume ratio and the enhanced catalytic activity of the nanocatalyst compared to its bulk counterpart [1–3]. A key objective of nanocatalysis is to produce catalyst with 100% selectivity, extremely high activity, low cost, and especially long-time stability [4,5]. Cobalt (Co), as a much more abundant element in the earth's crust than noble metals, has been intensively studied because of its relatively low cost and very potent catalytic properties in many important reactions [6–9]. However, compared to the noble-metal catalysts, Co nanoparticles (NPs) are much more easier to be oxidized in air, and thus leads to the deactivation and poor recycle stability especially when a long interval between two recycle applications is needed, which seriously limits their practical applications [10,11]. Current methods to overcome this problem are focused on coating Co NPs with some robust outer shells, such as silica, carbon, transition-metal oxides and so on [12–15], or applying and storing the catalysts under inert atmosphere [16]. However, these methods suffer from more or less drawbacks like modestly catalytic activity (due to the occupation of active sites by coating materials), complicated and uneconomical process for catalyst preparation and application [12–16]. Thereafter, exploring new strategies to effectively avoid the deactivation of Co NPs is highly desirable but still a big challenge.

With greenhouse gas emissions affecting environmental climates, the need for alternative fuels has become abundantly clear. Hydrogen has emerged as secure, renewable, inexhaustible, emission-free fuel [17]. However, finding efficient and safe hydrogen storage materials remains one of the most difficult challenges on the way to the fuel cell based hydrogen economy [18–20]. Ammonia borane (NH_3BH_3, AB) has been considered as a

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potential hydrogen storage material because of its high hydrogen content (19.6 wt%), high solubility and stability at room temperature and nontoxicity [21–25]. Recently, Co NPs have attracted an increasing level of attentions as catalysts for hydrogen generation from hydrolysis of AB owing to their high activities and low cost [26–28]. Although Co NPs are not easily to be oxidized under a reductive atmosphere of AB aqueous solution during the reaction, the big hurdle for their practical application also lies on their easy oxidative deactivation if for the recycle application with a long-time interval in water and air [29].

Ideally, when nanocatalysts are recycling applied, their activities are well maintained as high as those of the fresh catalysts. Therefore, refreshing the nanocatalysts may be a promising solution to recover the high activities of catalysts in recycles applications. Herein, by intentionally taking advantage of the readily oxidizable character of Co NPs in air, we describe a simple but efficient method to overcome the above obstacle of Co NPs. The concept lies on the facile, free, as well as reverse conversion between Co^0 NPs and Co^{2+} cations. Namely, oxidizes Co^0 completely into Co^{2+} for the long-time and oxygen-fearless storage, and reduces Co^{2+} back to fresh and highly active Co^0 for the recycle application. In the overall experiments, $NaBH_4$ is used as the reducing agent. To the best of our knowledge, the present metal-ion conversion is a novel way to successfully prevent the deactivation of nanocatalysts.

2. Experimental methods

2.1. Chemicals

Ammonia borane (AB, Aldrich, 90%), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, Beijing Chemicals Works, >99%), ammonium chloride (NH_4Cl, Beijing Chemicals Works, >99%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd, >96%), and ammonia solution (NH_4OH, Beijing Chemicals Works, 25%–28%) are used without further purification.

2.2. Characterization

Transmission electron microscope (TEM) (Tecnai F20, Philips) was applied for the detailed microstructure and composition information. The TEM samples were prepared by depositing one or two droplets of the NPs suspended in aqueous solution onto the amorphous carbon coated copper steel grids, which were then dried in argon (Ar) atmosphere. Ultraviolet and visible (UV–Vis) absorption spectra were recorded on an Agilent Cary 50 spectrophotometer in the wavelength range of 350–750 nm. Powder X-ray diffraction (XRD) patterns were performed on a Rigaku RINT-2000 X-ray diffractometer with Cu Kα. X-ray photoelectron spectrometry (XPS) analyses were carried out on an ESCALABMKLL X-ray photoelectron spectrometer using an Al Kα source.

2.3. Synthesis and reverse metal-ion conversion of Co system

Typically, 50 mg of AB and 10 mg of $NaBH_4$ was dissolved in 5 mL of distilled water, then $CoCl_2$ aqueous solution (0.006 M, 5 mL) was added into the above solution with magnetic stirring, and the black Co NPs were rapidly generated.

After the reaction, the black suspension (pH = 9.4) was magnetic stirred in air to oxidative etch the Co NPs. After 30 min of etching, the black suspension was changed into the pink solution. Then, the same amount of reducing agent as the initial experiment ($NaBH_4$ 10 mg, AB 50 mg) was readded into the pink solution to get the black Co NPs again. Such mental-ion conversion can be repeated freely for at least 20 times. All the reactions were performed at room temperature (293 K).

The above metal-ion conversion was traced by UV–Vis spectra. The initial-generated Co NPs was analyzed by XPS, and the reaction solution without Co NPs was used for UV–Vis analysis. To investigate the stability of the reformed pink solution, the solution was stored in air for two months, and then UV–Vis was performed on this solution again.

To find the impact factors on the metal-ion conversion, the following three experiments were applied: (1) Etching the Co NPs under Ar atmosphere. $CoCl_2$ (0.006 M, 5 mL) was purged with Ar for 1 h, and then 5 mL of aqueous solution containing the mixture of the $NaBH_4$ (10 mg) and AB (50 mg) was added into the above solution in Ar with 200 min. (2) Etching the pure Co NPs dispersed in distilled water in air. After the initial generation of Co NPs, they were separated from the reaction solution and washed by distilled water for several times, and then 10 mL distilled water was added into the pure Co NPs. Finally, the black suspension without ions was magnetic stirred in air for 200 min. (3) Etching the pure Co NPs dispersed in ammonia solution in air. After the initial generated of Co NPs, they were separated and washed, and then, 10 mL of distilled water was added into the pure Co NPs. The pH value of the black suspension was changed to 9.4 (as the initial reaction solution) by adding ammonia solution. Finally, the above suspension was magnetic was magnetic stirred in air for 200 min.

2.4. Heat treatment of the initial-generated Co NPs

After the initial-generated Co NPs were separated from the reaction solution and dried in Ar atmosphere, they were transferred into a furnace where a continuous Ar gas flow was introduced. Then, the furnace temperature was elevated to 873 K and maintained for 3 h. The as-obtained Co sample after heart treatment was used for XRD analysis.

2.5. Catalytic activity and recycle application of Co NPs

5 mL of aqueous solution containing $NaBH_4$ (10 mg) and AB (50 mg) was kept in a two-necked round-bottom flask. One neck was connected to a gas burette, and the other was connected to a pressure-equalization funnel to introduce $CoCl_2$ aqueous solution (0.006 M, 5 mL). The hydrogen generation reaction was begun once the $CoCl_2$ solution was added into the round-bottom flask containing AB and $NaBH_4$ solution with magnetic stirring. The evolution of gas was monitored using the gas burette. The hydrolysis of AB can be briefly expressed as follow:

$$NH_3BH_3 + 2H_2O = NH_4^+ + BO_2^- + 3H_2$$

After the hydrolysis reaction catalyzed by the *in situ* prepared Co NPs was completed, the reaction solution was stirred in air to etch the Co NPs. 30 min later, the clear pink solution containing regenerated Co^{2+} actions was obtained, and this pink solution was then stored in air for 7 days. After the long-time storage in air, the same amount of $NaBH_4$ and AB as the first time was readded into the pink solution to regenerate the Co NPs, and the recycle activity of the regenerated Co NPs to AB hydrolysis was tested again.

The above recycle tests were performed for 10 times (63 days). The initial-generated and the 10th regenerated Co NPs were used for TEM and XRD analyses. To save the experimental time and further characterize the recycle stability of Co NPs, another 10 times (10 days) of recycle tests with every interval of 1 day were continued to apply on the above 10th regenerated Co NPs in air at 293 K.

For comparison, the initial-generated Co NPs were washed and stored in 10 mL of distilled water for 7 days to mostly avoid the oxidative etching of Co NPs. After 7 days, AB (50 mg) was added into