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Graphene supported cobalt(0) nanoparticles for hydrolysis of ammonia borane

Lan Yang [a], Nan Cao [a], Cheng Du [a], Hongmei Dai [a], Kai Hu [a], Wei Luo [a,b,*], Gongzhen Cheng [a]

[a] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, PR China*
[b] *Suzhou Institute of Wuhan University, Suzhou, Jiangsu 215123, PR China*

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ABSTRACT

Cobalt(0) nanoparticles supported on graphene have been synthesized via a one-step *in situ* procedure, using the mixture of ammonia borane (AB) and sodium borohydride ($NaBH_4$) as the reducing agents under ambient temperature. Compared with $NaBH_4$, the as-prepared Co/graphene NPs which reduced by the mixture of $NaBH_4$/AB exhibit superior catalytic activity towards the hydrolytic dehydrogenation of AB. A kinetic study shows that the catalytic hydrolysis of AB is first order with respect to the concentration of the as as-synthesized NPs. The turnover frequency (TOF) is 13.8 mol H_2 min^{-1} $(mol\ Co)^{-1}$, which is higher than most of the non-noble metal catalysts, and even noble-metal based NPs. The activation energy has been measured to be 32.75 kJ mol^{-1}, which is lower than many reported values for the catalytic hydrolytic dehydrogenation of ammonia borane.

1. Introduction

Ammonia borane (NH_3–BH_3, AB) has been widely recognized as a highly favorable hydrogen storage material for fuel cell application, because of its 19.6 wt% hydrogen content, and its highly stable and environmentally benign [1–3]. The methods for decomposition of AB include thermal [4], catalytic hydrogen release in non-aqueous solvents [5] and hydrolysis [6]. Among them, the catalytic hydrolysis of AB appears to be the most convenient way [7], which could provide 3 mol of H_2 per mol AB with suitable catalyst at ambient condition. In the last few years, lots of potential catalysts have been reported in the literatures, including transition-metals [8], non-noble metals [9], noble metals [10], solid acids [11], metal oxides [12], boron-containing nanocomposites [12], and so on. The noble metal-based NPs have been identified to be effective for catalytic hydrolysis of AB, however, their high price and limited abundance hinder their practical applications. Therefore, it is promising to develop the catalytic activity of non-noble metal based catalysts, even to the level of noble-metal based catalysts.

Graphene, a single-atom-thick carbon material, has attracted much attention due to its excellent electronic, optical, chemical, mechanical properties, and large specific surface area, which could be an ideal substrate for growing and loading metal NPs. The graphene sheets can coat the surface of metal NPs, and thus the aggregation of the NPs would be prohibited, and the catalytic activity of them would be enhanced [13]. Herein, we report a facile *in situ* synthesis of Co NPs supported on graphene, which exhibit high catalytic activity and satisfied durable stability and magnetically recyclability for the hydrolysis of AB.

2. Experimental

The detailed experimental process could be found in the Supplementary material.

3. Results and discussion

Synthesis and characterization: The graphene supported Co NPs were prepared by adding the mixture of $NaBH_4$ and AB into the precursor solution containing $CoCl_2$ and graphene oxide (GO) at room temperature. The microstructure of Co/graphene NPs was fully analyzed by TEM and energy dispersive X-ray spectrometry (EDS) observations. As shown in Fig. 1a and b, the as-synthesized NPs were well dispersed on graphene, which help to prevent the agglomeration. The samples are basically amorphous, which have been reported to result in the high concentration of active sites of Co for the catalytic activity [14]. The EDS spectrum in Fig. 1e confirms the presence of Co. The XRD pattern of the as-prepared NPs and the annealed samples are displayed in Fig. S1. GO is successfully reduced to graphene since the peak of GO (001) at around 8.4° is disappeared, and a new peak at around 22.5° is observed in the as-prepared NPs, which corresponds to the peak of graphene (002). The as-prepared NPs have no obvious peak of Co, implying the sample is almost in an

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* Corresponding author at: College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, PR China. Tel.: +86 2787467716.
E-mail address: wluo@whu.edu.cn (W. Luo).

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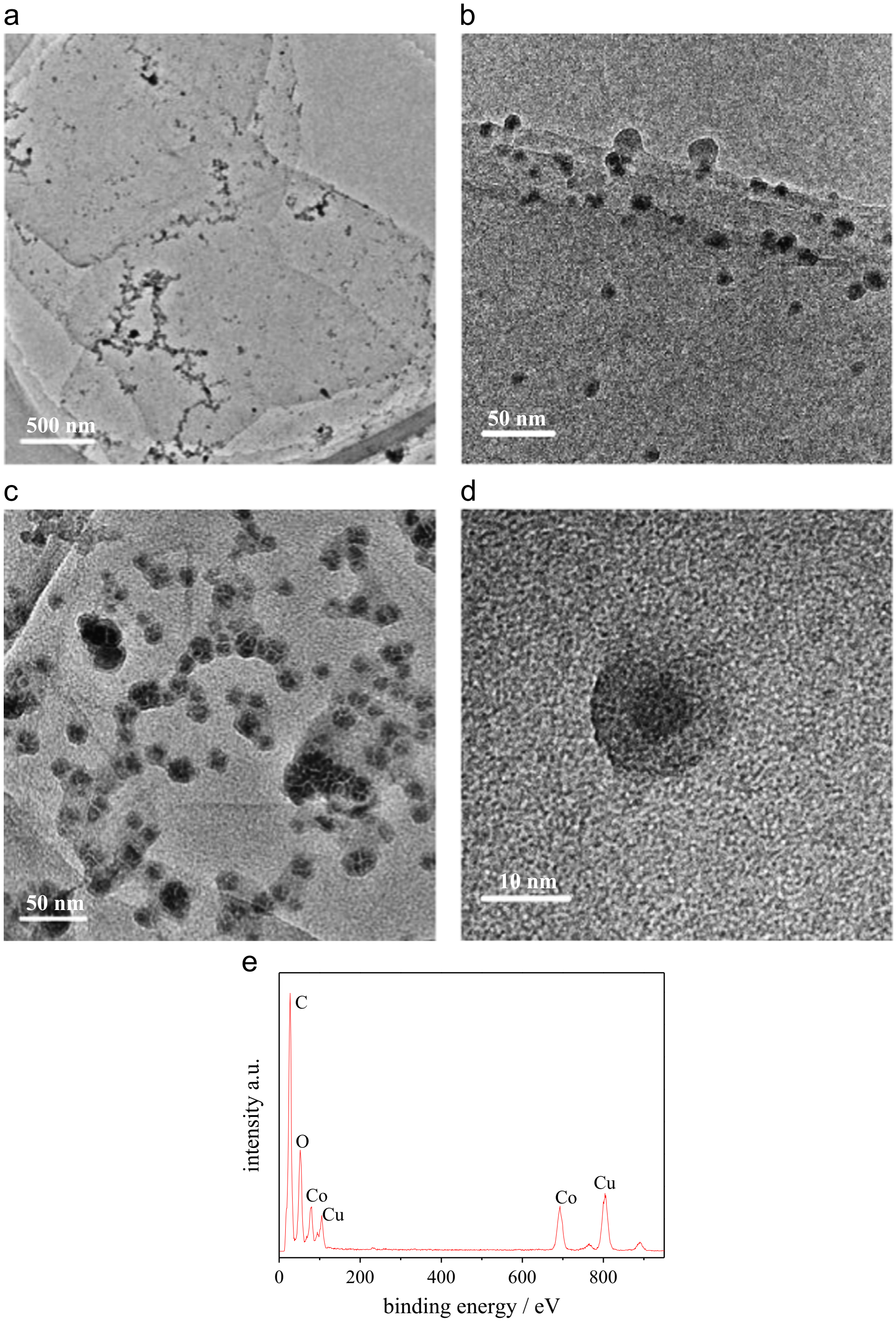

Fig. 1. (a,b) TEM images of Co/graphene NPs, (c,d) TEM and HRTEM images of Co/graphene NPs after five cycles, (e) EDS spectrum of Co/graphene NPs.

amorphous state, which is in good agreement with the TEM results. After annealed at 500 °C for 4 h under N_2 in tube furnace, the peak of Co (111) and Co (200) are found. Fig. 2 shows the X-ray photoelectron spectroscopy (XPS) of the GO and Co/graphene. Compared with the peaks of GO (Fig. 2a), the intensities of the oxygen containing functional groups (such as –C–O, –C=O, –COO) in Co/graphene (Fig. 2b) decrease significantly, which reveal the reduction of GO [15]. Fig. 2c shows the peak of Co 2p of the catalysts. There are two peaks whose peak tops were 778.1 and 781.5 eV, which stand for zero valent cobalt and cobalt oxide [16,17,18]. The formation of the oxidized cobalt most likely occurs during the sample preparation process for XPS measurements [15]. In the Raman spectroscopy (Fig. S2), the GO and graphene supported NPs exhibit two peaks centered at 1358 and 1596 cm^{-1}, corresponding to the D and G bands of the carbon products, respectively. After loading of the Co NPs, the I_D/I_G of the sample is increased from 1.03 to 1.31. The relative changes in the D to G peak intensity ratio confirm the reduction of GO during the *in situ* fabrication. Fig. S3 shows the FTIR spectra of GO and Co/graphene NPs. It can be seen clearly that the disappearance of C=O peak at 1732 cm^{-1} and the C–O peak at 1054 cm^{-1} of GO after the formation of graphene supported NPs, further indicating the GO was reduced to graphene during the process.

Catalytic activity for hydrolysis of AB by Co/graphene NPs: For comparison, Co/graphene NPs generated by the mixture of $NaBH_4$