



Short communication

Promoting hydrolysis of ammonia borane over multiwalled carbon nanotube-supported Ru catalysts via hydrogen spillover



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ABSTRACT

Multi-walled carbon nanotubes were used to deposit Ru metal by electrostatic adsorption and incipient wetness impregnation methods, respectively. The electrostatic adsorption method led to small (1.8–2.5 nm) and highly dispersed (0.51–0.72 dispersion) Ru metal nanoparticles. The initial hydrogen generation turnover rates over Ru catalysts with different metal particle sizes showed that ammonia borane hydrolysis reaction is structure-sensitive; large Ru particles displayed high turnover rates. Multiwalled carbon nanotube-supported Ru nanoparticles exhibit high turnover rate and low activation energy for the hydrolysis of ammonia borane because of hydrogen spillover effect associated with strong interaction between Ru metal and carbon nanotubes.

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1. Introduction

Ammonia borane (AB, NH_3BH_3) has been recognized as a chemical hydrogen storage material with high potential [1,2]. At present, two methods are used to release hydrogen: solid thermolysis and solvolysis (hydrolysis or methanolysis) [1–3]. In general, catalytic hydrolysis of AB has been widely studied because of hydrogen capacity of up to 19.5 wt% of AB and H_2O under ambient atmosphere at room temperature with the aid of efficient catalysts. The design and synthesis of efficient hydrolysis catalysts has attracted increasing attention in the last decade [4].

To date, the noble metals (Pd [5], Pt [6,7], Ru [8–25], Rh [4,26], Ag [27] and Au [28]), the transition metals [4,29–33]), and bimetallic [34] and alloy [35] catalysts have been reported to be active catalysts for the hydrolysis of AB. Among these catalysts, Ru-based catalysts have proved to be the most efficient catalysts for hydrolysis of borohydrides and are also frequently used in AB hydrolysis [8–25]. Xu et al. found that Pt nanoparticles on different supports ($\gamma\text{-Al}_2\text{O}_3$, carbon and SiO_2) possess different hydrolysis activity, and this is mainly attributed to differences in particle size [3]. Interestingly, the activity of AB hydrolysis over Ru metal nanoparticles with similar size (~2 nm) varied with the type of support used (carbon, carbon nanotubes, metal oxides, etc.) [8–25]. In particular, carbon materials seem to show better performance

for Ru catalysts [17,23]. These observations suggest an important role of supports in determining the nature and performance of Ru-based catalysts. In fact, promotion of hydrogenation by hydrogen spillover has been observed on carbon nanotube-supported metal nanoparticles [36]. Moreover, metal-doped carbon nanotubes possess good hydrogen storage capacity under ambient pressure [37,38]. We infer that hydrogen spillover associated with the excellent hydrogen storage capacity of carbon nanotubes on the supported metal catalyst would promote its catalytic performance in the hydrolysis of AB. Here, various Ru nanoparticles supported on multi-walled carbon nanotubes (MWCNTs), activated carbon (AC), and SiO_2 were prepared and studied to verify our inference.

2. Experimental

2.1. Catalyst synthesis

MWCNTs and AC were treated in boiling water for 12 h and then dried at 383 K for 12 h. Silica was treated in ambient air at 673 K for 3 h. Ru metal was deposited on supports using electrostatic adsorption (EA) protocols [39], which added supports to an aqueous solution of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ and NaOH. After stirring for 1 h (pH = 11), the solids were filtered and washed with deionized water to remove chloride ions. The samples were dried at 383 K for 24 h. To obtain MWCNT- and AC-supported Ru catalysts, the samples were added to AB solution (0.1 mol L^{-1} , solid/liquid weight ratio = 1/10) with stirring

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(500 rpm) while flowing nitrogen gas to the solution (50 mL min^{-1}) for 1 h. The resulted catalysts were collected and washed three times with deionized water. For comparison, Ru catalysts supported on MWCNTs and AC were also prepared by a modified incipient wetness impregnation (IWI) method (See supplementary material).

The catalysts prepared using EA and IWI methods are denoted as Ru/MWCNTs-EA and Ru/MWCNTs-IWA, respectively.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of catalysts were obtained over a 2θ range of $30\text{--}80^\circ$ at a scan rate of 4° min^{-1} on a Rigaku D/max 2500 X-ray diffractometer ($\text{Cu K}\alpha$, $\lambda = 1.54178 \text{ \AA}$) operated at 40 kV and 40 mA. The compositions of samples were determined through inductively coupled plasma atomic emission spectrometry (ICPAES) using an IRIS Intrepid spectrometer. The morphology and particle size were examined via transmission electron microscopy (TEM) using a FEI Tecnai G2 high-resolution transmission electron microscope operated at 200 kV. Ru dispersion was determined from the uptake of strongly chemisorbed hydrogen at 313 K using a Quantasorb chemisorption analyser (Quantachrome Corp.) [39].

2.3. Hydrolysis reactions

The hydrolysis reaction was performed in a small glass reactor (200 mL) in a bath-type hydrogen generator [40]. The mass-transfer limitations were excluded using procedures described elsewhere [40]. A typical measurement consisted of introducing the catalyst (0.0050–0.10 g) into the reactor along with a solution containing NH_3BH_3 . The hydrogen generation rate (mL min^{-1}) was measured using a hydrogen flow meter. The initial hydrogen generation rate was recorded, and the initial hydrogen generation turnover rate (per surface metal atom, as determined from the chemisorption uptake) was calculated ($\text{mol}_{\text{H}_2} \text{ mol}_{\text{surf-metal}}^{-1} \text{ s}^{-1}$).

Typically, a certain amount of Ru catalysts was placed in a bath-type hydrogen generator (200 mL). Then, a 10% H_2/He gas mixture was induced to replace the air in the generator. The Ru catalysts were then treated at 473 K for 2 h to reduce the ruthenium oxide species formed on the surface of Ru metal clusters during the transfer of the Ru catalysts into generator. After cooling to room temperature, 50 mL of deionized water was injected to disperse the Ru catalysts under stirring at 500 rpm. Then, pure He gas was induced to replace the 10% H_2/He gas, and the mixture was heated to the reaction temperature. The hydrogen generator was equipped with an outlet tube connected to a column packed with silica gel to eliminate any moisture formed. A mass flow meter was used to record instantaneous hydrogen generation rates (mL min^{-1}).

The hydrolysis reaction was conducted by injecting an AB aqueous solution using a high precision syringe and the instantaneous hydrogen generation rate was recorded digitally at 1 s interval. The instantaneous hydrogen generation rate increased into a maximum value within 30 s and then stabilized for tens of minutes. The maximum hydrogen generation rate (r_{max} , mL min^{-1}) was considered as the initial hydrogen generation rate for calculating initial hydrogen generation turnover rate (TOR) based on the following equation.

$$\text{TOR} = \frac{r_{\text{max}}}{22.4 \times 1000 \text{ mL} \cdot \text{mol}^{-1} \times 60 \text{ s} \cdot \text{min}^{-1}} \times \frac{1}{n_{\text{surf-Ru}}}$$

where $n_{\text{surf-Ru}}$ is the amount of surface active Ru metal (mol) used in each hydrolysis reaction calculated from the metal dispersion of Ru catalysts, the weight of Ru catalysts and the Ru metal loading [39].

3. Results and discussion

3.1. Catalyst properties

A comparison of XRD patterns of MWCNTs and Ru/MWCNTs catalysts, presented in Fig. 1, clearly shows no change in the characteristic diffraction peaks of multiwalled carbon nanotubes after deposition of Ru metal, as found in the work of Özkar et al. [12]. The diffraction peaks at 26.2 and 43.3° could be well-indexed as (002) and (110) reflections of graphite structure, respectively. The XRD patterns of MWCNTs, Ru/MWCNTs-EA (1.0 wt% Ru, Table 1) and Ru/MWCNTs-IWI-1 (0.9 wt% Ru, Table 1) are essentially the same. There are not any observable diffraction peaks attributable to Ru metal in Ru/MWCNTs-EA, Ru/MWCNTs-IWI-1 or Ru/AC-EA samples, probably as a result of low Ru loading and small Ru cluster size. A weak peak corresponding to (101) plane of Ru metal could be distinguished in the XRD pattern of Ru/MWCNTs-IWI-2 (JCPDS No. 1-1253) at higher metal loading (5.0 wt% Ru), suggesting the formation of larger Ru clusters.

Table 1 shows metal loadings and metal dispersions of catalysts. Clearly, samples obtained by EA method possess a higher Ru dispersion than catalysts obtained by IWI method. This indicates an advantage in the synthesis of small metal clusters using EA method. Fig. 2 shows the TEM and HRTEM images of supported Ru catalysts. Most of Ru nanoparticles are located on the external surface of MWCNTs without incorporating into the pores of MWCNTs. Ru particles of $\sim 2 \text{ nm}$ are highly dispersed over Ru/MWCNTs-EA, and clear lattice fringes in the HRTEM images indicate the formation of metallic Ru. Compared to Ru/MWCNTs-EA samples, Ru/MWCNTs-IWI shows a homogeneous distribution of larger nanoparticles ($\sim 3 \text{ nm}$) on supports. As shown in Table 1, size of Ru nanoparticles observed in TEM images is similar to the size calculated from chemisorption results. These indicate a narrow size distribution of Ru particles over supports. In addition to MWCNT-supported Ru nanoparticles, Ru/AC and commercial Ru/C catalysts also show a homogeneous distribution of Ru nanoparticles.

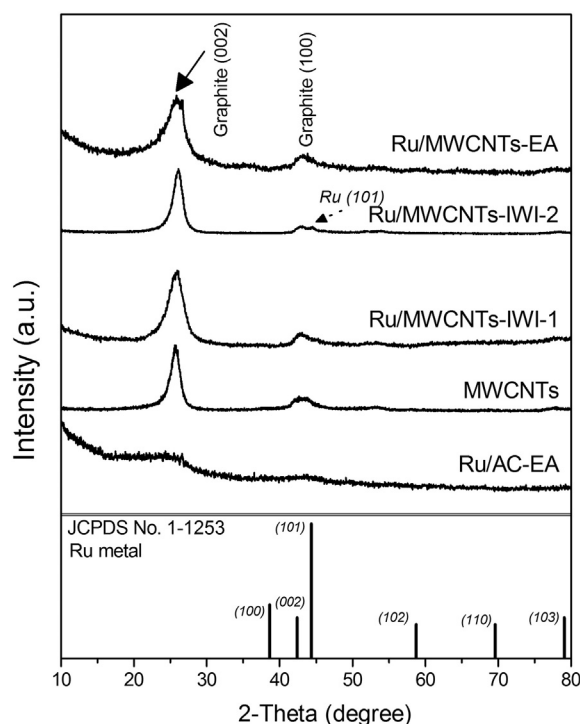


Fig. 1. XRD patterns of MWCNTs and supported Ru catalysts.

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