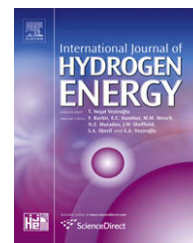


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# Water soluble laurate-stabilized ruthenium(0) nanoclusters catalyst for hydrogen generation from the hydrolysis of ammonia-borane: High activity and long lifetime

Feyyaz Durap<sup>\*,1</sup>, Mehmet Zahmakıran, Saim Özkar

Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

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## ABSTRACT

The simplest amine-borane, considered as solid hydrogen storage material, ammonia-borane ( $\text{H}_3\text{NBH}_3$ ) can release hydrogen gas upon catalytic hydrolysis under mild conditions. Herein, we report the preparation of a novel catalyst, water dispersible laurate-stabilized ruthenium(0) nanoclusters from the dimethylamine-borane reduction of ruthenium(III) chloride in sodium laurate solution at room temperature. The ruthenium nanoclusters in average size of  $2.6 \pm 1.2$  nm were isolated from the solution and well characterized by using TEM, XPS, FTIR, and UV-visible electronic absorption spectroscopy. The water dispersible laurate-stabilized ruthenium(0) nanoclusters were found to be highly active and long-live catalyst with a TOF of 75 mol  $\text{H}_2$ /mol Ru · min and TTO value of 5900 mol  $\text{H}_2$ /mol Ru in the hydrolysis of ammonia-borane at  $25.0 \pm 0.1$  °C.

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## 1. Introduction

There have been intensive efforts for developing safe and efficient methods for hydrogen storage, a key issue of the hydrogen economy [1–3]. Amine-boranes have recently been considered among the hydrogen storage materials because of the following advantageous properties [4]: (i) having high hydrogen content, (ii) having high stability, and (iii) being environmentally benign. The simplest amine-borane being considered as solid hydrogen storage material [5–8] is ammonia-borane (AB,  $\text{H}_3\text{NBH}_3$ ) possessing a low molecular weight (30.9 g/mol) and highest hydrogen content (19.6 wt%) [4]. AB is nontoxic, stable, and environmentally benign, can be handled at room temperature and can release hydrogen gas

upon catalytic hydrolysis under mild conditions (Eq. (1)) [4]. The hydrolysis occurs at appreciable rate only in the presence of a suitable catalyst at ambient temperature [9,10].



So far, the catalysts tested in the hydrolysis of ammonia-borane are platinum supported on carbon (20 wt%) [10], colloidal rhodium(0) [11],  $\text{Ni}_{1-x}\text{Pt}_x$  hollow spheres [12], ruthenium(0), rhodium(0) and platinum(0) particles supported on  $\gamma\text{-Al}_2\text{O}_3$  [13], various transition metal salts  $\text{RuCl}_3$ ,  $\text{PdCl}_2$ ,  $\text{CoCl}_2$ , and palladium supported carbon (Pd/C) [14], Fe(0) nanoparticles [15], Co(0)/ $\text{Co}_2\text{B}$ , Ni(0)/ $\text{Ni}_3\text{B}$ , Cu(0) nanoparticles [16], poly(*N*-vinyl-2-pyrrolidone) (PVP) stabilized nickel catalyst [17], hollow Ni- $\text{SiO}_2$  nanosphere [18] and

\* Corresponding author. Tel.: +312 210 3212; fax: +312 210 5135.

E-mail address: [fdurap@dicle.edu.tr](mailto:fdurap@dicle.edu.tr) (F. Durap).

<sup>1</sup> On the leave of absence from Department of Chemistry, Dicle University, 21280 Diyarbakır, Turkey.

Pt- and Ni-based alloy catalysts [19]. The use of colloidal or supported particles as active catalyst in the hydrolysis of ammonia-borane implies that reducing the particle size can cause an increase in the catalytic activity as the fraction of surface atoms increases with the decreasing particle size [20]. Accordingly, the transition metal nanoclusters can be employed as catalyst for this reaction as well. For this purpose, the transition metal nanoclusters need to be stabilized to certain extent [21]. In the preparation of water-soluble transition metal nanoclusters, electrostatic stabilization by anions [22,23] is necessary to prevent their agglomeration into the bulk metal. Here we report, for the first time, the preparation and characterization of water dispersible ruthenium(0) nanoclusters stabilized by laurate (dodecanoate) anion and their employment as catalyst in the hydrolysis of ammonia-borane.

## 2. Experimental

Ruthenium(III) chloride trihydrate ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , 99.5%, Sigma), sodium laurate ( $\text{C}_{12}\text{H}_{23}\text{NaO}_2$ , 99%, Fluka), dimethylamine-borane (DMAB) ( $(\text{CH}_3)_2\text{NHBH}_3$ , 97%, Sigma), and ammonia-borane (AB,  $\text{H}_3\text{NBH}_3$ , 99%, Sigma) were purchased from Aldrich. Ethanol was purchased from Merck. Deionized water was distilled by water purification system (Milli Q-pure WS). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at  $150^\circ\text{C}$ .

### 2.1. The preparation of laurate-stabilized ruthenium(0) nanoclusters

Ruthenium(III) chloride trihydrate of 4.2 mg ( $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , 0.02 mmol) was dissolved in 10 mL deionized water and 44.5 mg sodium laurate ( $\text{C}_{12}\text{H}_{23}\text{NaO}_2$ , 0.2 mmol) was added into this solution and stirred half an hour at room temperature. Then 59 mg dimethylamine-borane ( $(\text{CH}_3)_2\text{NHBH}_3$ , 1.0 mmol) was added into this mixture, after 4 h the color of solution completely changed into deep brown at room temperature. The laurate-stabilized ruthenium(0) nanoclusters, dark brown in color, were found to be stable in aqueous media (no precipitation was observed after a month of storage) under ambient conditions.

### 2.2. The separation of laurate-stabilized ruthenium(0) nanoclusters as a solid material

The laurate-stabilized ruthenium(0) nanoclusters were separated from the solution by precipitation with ethanol (20 mL) followed by centrifugation (5000 rpm, for 1 h). The laurate-stabilized ruthenium(0) nanoclusters were separated as a solid material washed with 30% (v/v) water/ethanol mixture to remove water soluble impurities.

### 2.3. Transmission electron microscopy (TEM) analyses

One drop of the laurate-stabilized ruthenium(0) nanoclusters solution was deposited on the chloroform cleaned, carbon coated Cu TEM grid and the solvent was then

evaporated and analyzed by using Philips CM-12 TEM with a  $70\ \mu\text{m}$  lens operating at 100 kV and with a  $2.0\ \text{\AA}$  point-to-point resolution. Samples were examined at magnification between 100 and 400K. Particle size analysis was performed using the public domain NIH Image J 1.62 program developed at the U.S. National Institutes of Health and available on the Internet at <http://rsb.info.nih.gov/ni-image/>. For each particle, the diameter was calculated from the area by assuming that the nanoclusters are spherical. Size distributions are quoted as the mean diameter  $\pm$  the standard deviation.

### 2.4. X-ray photoelectron spectroscopy (XPS) analyses

The XPS analysis was performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al  $K\alpha$  radiation (1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV). The peak fitting of original spectrum has been done by mixing (50:50%) of both Lorentzian and Gaussian functions on Origin 7.0 program.

### 2.5. Fourier transform infrared spectroscopy (FTIR) analyses

The sample prepared for the XPS analysis was also used for the FTIR analysis. FTIR spectrum of both sodium laurate and the laurate-stabilized ruthenium(0) nanoclusters was taken from KBr pellet on a Nicolet 510 FTIR Spectrophotometer using Omnic software.

### 2.6. $^{11}\text{B}$ NMR analyses

$^{11}\text{B}$  NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz for  $^{11}\text{B}$ .  $\text{D}_2\text{O}$  and  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  were used as a lock and an external reference, respectively. At the end of the hydrolysis reaction, the resulting solutions were filtered and the filtrates were collected for  $^{11}\text{B}$  NMR analysis.

### 2.7. Method for testing the catalytic activity of laurate-stabilized ruthenium(0) nanoclusters in the hydrolysis of $\text{H}_3\text{NBH}_3$

The catalytic activity of laurate-stabilized ruthenium(0) nanoclusters in the hydrolysis of ammonia-borane was determined by measuring the rate of hydrogen generation. To determine the rate of hydrogen generation the catalytic hydrolysis of ammonia-borane was performed using a Fischer–Porter pressure bottle modified with Swagelock TFE-sealed quick connects and connected to an Omega PX-302 pressure transducer interfaced through an Omega D1131 digital transmitter to a computer using the RS-232 module. The progress of an individual hydrolysis reaction was followed by monitoring the increase of  $\text{H}_2$  pressure on Lab View 8.0 program. The pressure versus time data was processed using Microsoft Office Excel 2003 and Origin 7.0 then converted into the proper unit [volume of hydrogen (mL)]. In a typical experiment, 30.9 mg (1 mmol)  $\text{H}_3\text{NBH}_3$  was dissolved in 10 mL water, (corresponding to a maximum amount of 3 mmol = 67 mL  $\text{H}_2$  at  $25.0 \pm 0.1^\circ\text{C}$ ). This

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