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Controlled galvanic replacement of Ni in $Ni(OH)_2$ by Pd: A method to quantify metallic Ni and to synthesize bimetallic catalysts for methanol oxidation

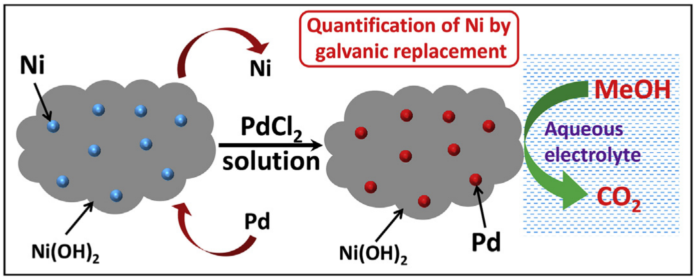
Sisir Maity[a], Srinivasan Harish[a,b,1], Muthusamy Eswaramoorthy[a,*]

[a] Nanomaterials and Catalysis Lab, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur P.O., Bengaluru, 560064, India
[b] Department of Chemistry, PSG Institute of Technology and Applied Research, Coimbatore, 641062, India

HIGHLIGHTS

- A new method to estimate the amount of metallic Ni quantitatively in $Ni(OH)_2/Ni$.
- Bimetallic NiPd was synthesized on $Ni(OH)_2$ by galvanic replacement of Ni by Pd.
- Catalysts show better activity towards methanol oxidation than commercial Pd/C.

GRAPHICAL ABSTRACT



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ABSTRACT

We have demonstrated a new and simple methodology to quantify the amount of metallic Ni present in the mixed nickel hydroxide/nickel surface using galvanic replacement reaction. This method was also used to manipulate the formation of nanocomposite, NiPd on $Ni(OH)_2$ support by controlling the extent of galvanic replacement of Ni by Pd. The bimetallic NiPd nanoparticles supported on $Ni(OH)_2$ prepared by galvanic reaction showed better electrocatalytic activity for methanol oxidation than commercial Pd/C. This approach can be extended to synthesize various nickel containing bimetallic nanoparticles essential for different catalysis.

1. Introduction

Bimetallic NiPd catalysts gained a lot of attention in recent years owing to their improved performance than the Pd catalysts in many industrially significant reactions such as hydrogen evolution reaction [1,2], oxygen reduction reaction [3,4], formic acid oxidation [1,5–7], methanol oxidation [8–12] and direct synthesis of hydrogen peroxide [13]. One of the methods often used to obtain NiPd nanostructure is the borohydride reduction of Ni and Pd salt precursors [9,13–17]. In borohydride reduction, although Pd salt is fully reduced to Pd nanostructure, Ni salt mostly gets converted to $Ni(OH)_2$ and Ni due to higher pH associated with the addition of borohydride [9,13]. As a corollary, the obtained nanostructures mostly composed of $Ni(OH)_2$ and Ni nanoparticles in addition to NiPd bimetallic nanoparticles. Quantification of metallic Ni present in the $Ni(OH)_2$ is one of the challenging tasks, although metallic Ni (in zero oxidation state) can be analyzed using magnetic measurement due to its ferromagnetic behaviour [13]. The Ni nanoparticles in $Ni(OH)_2$ can be further estimated by converting it into

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[*] Corresponding author.
E-mail address: eswar@jncasr.ac.in (M. Eswaramoorthy).
[1] Current address: Department of Chemistry, Sri Paramakalyani College, Alwarkurichi - 627412, India.

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Pd nanoparticles through galvanic replacement reaction [1,12]. This method not only allows us to estimate the total amount of Ni present in zero oxidation state in $Ni(OH)_2$, but also allows us to have a good control on the formation of NiPd bimetallic nanoparticles on $Ni(OH)_2$ support by controlling the time of galvanic replacement reaction.

In this work, we attempted to utilize high surface area porous $Ni(OH)_2/Ni$ nanostructure prepared by borohydride reduction method developed by our group [13,18] as a substrate for galvanic replacement reaction with Pd. The as-synthesized nanostructure, $Ni(OH)_2/Ni$ was used as a template for the galvanic replacement of Ni present in $Ni(OH)_2/Ni$ by Pd. The resulting NiPd loaded on $Ni(OH)_2$ nanostructure was tested for the electrocatalytic activity for methanol oxidation as the test reaction.

2. Experimental section

2.1. Materials and characterization techniques

$NiCl_2.6H_2O$, $NaBH_4$, NaOH and Methanol (AR grade) were purchased from S D Fine Chemicals; $PdCl_2$ and Nafion were purchased from Sigma Aldrich; and Pd/C (5 wt%) was purchased from Alfa Aesar. All the chemicals were used as such without any further purification.

Powder X-ray diffraction (PXRD) patterns were recorded using Bruker-D8 diffractometer using Cu Kα radiation, ($\lambda = 1.54$ Å, step size: 0.02, current: 30 mA and voltage: 40 kV). Field-emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDS) were obtained by using FEI (Nova-Nano SEM-600 Netherlands) equipment. Transmission electron microscope (TEM) imaging was done on a JEOL, JEM 3010 operated at 200 kV. Samples were prepared by putting a drop of very dilute dispersion in ethanol on a TEM grid (carbon polymer, 300 mesh). Inductively coupled plasma – atomic emission spectroscopy (ICP-AES) was carried out using a Perkin – Elmer Optima 7000 DV machine. Gas adsorption-desorption measurements were performed on Autosorb-iQ2 (Quantachrome corp.) at 77 K. The samples were degassed before starting the nitrogen gas sorption analysis under a high vacuum for 12 h at 373 K.

2.2. Synthesis of $Ni(OH)_2/Ni$ nanostructure

The $Ni(OH)_2/Ni$ nanostructure was synthesized via one step process by the reduction of aqueous $NiCl_2$ solution in presence of $NaBH_4$ at room temperature [1,2]. In a typical procedure, 20 mL 0.1 M aqueous solution of $NiCl_2$ was rapidly added to a 100 mL 0.1 M aqueous solution of freshly prepared $NaBH_4$ with vigorous stirring. The mixture was allowed to stir for 30 min. The solid product obtained after stirring was separated out and washed with water for several times and finally dried at 50 °C for overnight.

2.3. Galvanic replacement of Ni by Pd in $Ni(OH)_2/Ni$ nanostructure

In a typical procedure, 50 mg of as-synthesized $Ni(OH)_2/Ni$ nanostructure was soaked in 10 mL aqueous solution of 10 mM $PdCl_2$ solution with stirring for different time periods (5, 10, 30, 60 and 720 min). The solid product thus obtained was centrifuged and washed thoroughly with distilled water to make sure the complete removal of $PdCl_2$. Finally, the sample was dried at 50 °C for overnight. The Pd loading in all the galvanic replacement samples were analyzed by ICP-AES. The blank experiment was also carried out with $Ni(OH)_2/Ni$ in absence of $PdCl_2$ and no leaching of Ni from the sample was observed in the similar conditions.

2.4. Electrochemical measurements

All the electrochemical measurements were carried out using electrochemical work station obtained from CH instruments (660C, USA) using a three-electrode set-up. The measurements were carried out using long Pt-wire having large area as a counter electrode, mercury-mercuric oxide (MMO) electrode as a reference electrode in strong alkaline medium (1 M NaOH) and glassy carbon (GC) electrode having 3 mm diameter (geometric area 0.07068 cm^2) as working electrode. All the electrochemical experiments were carried out in deaerated solution by bubbling Ar gas for 30 min with a scan rate of 20 $mV\,s^{-1}$. The mass-current densities for all the samples are given with respect to the electrochemically active-mass calculated from Faraday's law.

2.5. Electrode preparation and methanol oxidation

2 mg of the sample was dispersed in a mixture of milli Q water (0.9 mL) and 5 wt % nafion (0.1 mL) solution and ultrasonicated to obtain a homogeneous catalyst ink. Then, 3 μL of the catalyst ink was drop casted on a cleaned glassy carbon (GC) electrode (3 mm diameter) with a catalyst loading of $\sim 0.085\ mg\,cm^{-2}$. The GC electrode was dried in ambient conditions and used as working electrode in the electrochemical studies. The methanol oxidation was carried out using 0.5 M methanol in 1 M aqueous solution of NaOH.

3. Results and discussion

The $Ni(OH)_2/Ni$ nanostructure was synthesized by reduction of $NiCl_2$ in presence of $NaBH_4$ (as discussed in the experimental section). This method produces mostly $Ni(OH)_2$ along with Ni nanoparticles as nickel is prone to hydrolyze to its hydroxide at higher pH produced by the presence of $NaBH_4$ [13]. The Ni nanoparticles dispersed in the $Ni(OH)_2$ nanostructure are difficult to detect using powder X-ray diffraction (PXRD) study and can't be quantified by inductively coupled plasma – atomic emission spectroscopic (ICP-AES) analysis [13]. The $Ni(OH)_2/Ni$ nanostructure shows a broad X-ray diffraction peak (Fig. 1a) which confirms the amorphous nature of the sample. The field emission scanning electron microscopy (FESEM) image of $Ni(OH)_2/Ni$ shows sponge like morphology (Fig. 1b).

Galvanic replacement (details in the experimental section in supplementary information) was carried out by soaking of $Ni(OH)_2/Ni$ in $PdCl_2$ salt solution (10 mM) at different periods of time (5, 10, 30, 60 and 720 min). During the galvanic replacement, Ni metal nanoparticles dispersed in $Ni(OH)_2$ nanostructure were replaced by Pd metal as the reduction potential of Pd^{2+}/Pd ($E^o = +0.915$ V) is higher than Ni^{2+}/Ni ($E^o = -0.25$ V). Since the galvanic replacement reactions occur with non-noble metal of zero oxidation state [19], the amount of metallic Ni present in the mixed metal hydroxide/metal surface can be directly correlated with amount of Pd (Table 1). The amount of Pd loading with time by galvanic replacement was quantitatively estimated by ICP-AES and the results are given in Table 1. From the table, it is observed that all the metallic Ni was replaced by Pd within 60 min which mostly corresponds to around 0.05 mol% of Ni present in $Ni(OH)_2$. Beyond 60 min time of galvanic replacement, no increase in the Pd loading confirmed from ICP-AES, suggesting that all the nickel (zero valent state) present in the as-prepared sample are replaced by Pd (Table 1).

The galvanic replacement reaction carried out for different time periods (10, 30, 60 and 720 min) shows diffraction patterns similar to that of Pd in Pd/C (Fig. S1 in supplementary information). FESEM analysis shows similar morphology as that of $Ni(OH)_2/Ni$ nanostructure for all the synthesized samples. $Ni(OH)_2/Ni_{0.25}Pd_{0.75}$ (after 30 min galvanic replacement) was chosen for further studies as it shows better electrocatalytic performance towards methanol oxidation among all the samples. The $Ni(OH)_2/Ni_{0.25}Pd_{0.75}$ (abbreviated later as $Ni(OH)_2/NiPd$) sample shows bright spots in FESEM (Fig. 2a) associated with Pd (lighter element Ni is replaced by heavier Pd). Further, the energy dispersive X-ray spectroscopic (EDS) analysis shows the presence of Pd distributed over the $Ni(OH)_2/NiPd$ nanostructure (Fig. 2a). The transmission electron microscopy (TEM) analysis of $Ni(OH)_2/NiPd$ (Fig. 2b) further confirms the Pd dispersion over $Ni(OH)_2$ nanostructure. The Pd particles are polydispersed in nature and the particles size are in the