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Transition metal phosphide catalysts for hydrogen oxidation reaction

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ABSTRACT

A series of transition metal phosphides consisting of tungsten (WP), cobalt (CoP), nickel (NiP), nickel–tungsten (Ni–WP), cobalt–tungsten (Co–WP) and cobalt–molybdenum (Co–MoP) was prepared by a temperature-programmed reduction process. Hydrogen oxidation activities for the phosphide compounds were studied. The hydrogen oxidation reaction (HOR) was determined using a half-cell rotating disc electrode in a 0.5 M H_2SO_4 electrolyte. In addition, the passivity of the phosphides in an acidic environment was studied by ICP. The Co–WP demonstrated the highest activity for the HOR based on chronoamperometry and the exchange current density. The single WP exhibited a low HOR activity, but the incorporation of Ni or Co enhanced the activity. In contrast, WP exhibited a high passivity, while NiP and CoP dissolved in the 0.5 M H_2SO_4. The high activities over Co–WP and Ni–WP were attributed to the role of WP in preventing the Co and Ni from corroding in the acidic media.

1. Introduction

Fuel cells utilize hydrogen gas to generate clean and useful energy by the electrocatalytic oxidation of hydrogen (HOR). At present, the best and most practical catalyst for the HOR is the Pt-alloy catalysts. However, because these catalysts are expensive, current studies are concentrated on exploring a more economical catalyst based on non-noble materials, for example, carbides and perovskites. One of the non-noble catalysts considered as a potential candidate is the transition metal phosphide, which is generally known to demonstrate excellent activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) in the petroleum industries. In addition to its activity, these materials exhibit excellent physical and mechanical properties [1–5], for instance, electric conductivity, hardness, wear and corrosion resistance. Recently, monometallic phosphides have been studied for their use in electrode reactions, porous anode catalysis and in Li electrodes [6]. Daimon and Kurobe [7] reported that the addition of phosphorus to Pt–Ru resulted in a higher catalytic activity due to the effective particle size reduction of Pt–Ru. Phosphides have also recently been used for methanol oxidation in DMFCs [8]. In the present study, we investigated the HOR activities for some single and binary phosphide compounds. The phosphides were also investigated for their resistivity in acidic media due to the highly acidic environment of the PEFC.

2. Experimental

2.1. Catalyst preparation

The precursors of the metal phosphides (WP, CoP or NiP) were prepared by combining stoichiometric quantities of ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$), cobalt nitrate ($Co(NO_3)_2\cdot nH_2O$) or nickel nitrate ($Ni(NO_3)_2\cdot nH_2O$) with an aqueous solution of diammonium phosphate ($(NH_4)_2HPO_4$). For the bimetallic phosphides (Ni–WP and Co–WP), ammonium metatungstate or ammonium molybdate was added to cobalt nitrate, ($Co(NO_3)_2\cdot nH_2O$) or nickel nitrate together with diammonium phosphate. As for the Co–MoP, the same starting material was used except that ammonium metatungstate was replaced with ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot nH_2O$). The bimetallic ratios of Ni to W, Co to W and Co to Mo were set constant at 1:1. The solids were dissolved in water at 313 K with stirring and then dried at 393 K. The catalysts were ground before being calcined for 5 h at 773 K. These oxide precursors were then reduced at temperatures shown in Table 1 at a ramping rate of 1 K min^{-1} in a stream of H_2 and maintained at the final temperature for 2 h. Prior to phosphidation, temperature-programmed reduction (TPR) was carried out in a flow of hydrogen, and the evolution of water ($m/z = 18$) was measured online using a quadrupole mass spectrometer (Baltzer). The mixture was then cooled and passivated under a stream of 1% O_2/He. The dissolution of the metal phosphides in acid was carried out by adding 2 mg of the catalyst to 10 mL of 0.5 M H_2SO_4, then followed by mixing in a tube mixer for 24 h prior to analysis by inductively coupled plasma spectroscopy (ICPS, Shimadzu).

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Table 1
The properties and HOR activities of the transition metal phosphides measured by a half-electrode cell, and the concentrations of the respective metals after mixing for 24 h in 0.5 M H_2SO_4 solution.

Metal phosphides	Reduction temperature (K)	BET area (m^2/g)	Exch. Curr. j_0 ($\mu A/cm^2$)	Oxidation current ($\mu A/\mu g$)	Conc. in 0.5 M H_2SO_4 (ppm)	
					Co or Ni	W or Mo
WP	923	9	2.01	0.0001	–	$1^{(W)}$
NiP	823	10	0.67	0.0010	$>100^{(Ni)}$	–
NiWP	873	10	2.46	0.0027	$6^{(Ni)}$	$1^{(W)}$
CoP	823	n.m.	n.m.	0.0030	$>100^{(Co)}$	–
CoWP	873	10	3.03	0.0087	$29^{(Co)}$	$4^{(W)}$
CoMoP	873	5	0.44	0.0041	$97^{(Co)}$	$51^{(Mo)}$

n.m.: not measured.

2.2. Characterization

The bulk structure of the phosphide catalyst was examined by XRD (30 kV, 28 mA). The diffraction pattern was obtained using an RINT2000 (Rigaku Co.) with Cu Kα radiation (λ = 1.542 Å). The peaks were identified by the JCPDS card references for WP (PDF#29-1364), NiP (PDF#03-953), CoP (PDF#32-0306), NiWP (PDF#47-1346) and CoMoP (PDF#32-299). The specific surface area of the catalyst was determined using an Omnisorp 100CX (Beckman Coulter Co.) at liquid nitrogen temperature after the catalyst was evacuated at 473 K for 2 h. XPS was performed by an ESCA-3200 (Shimadzu Corp.) using Mg Kα radiation at the power of 240 W (30 mA, 8 kV). The peak shift correction was based on the binding energies of C 1s (284.6 eV). The baseline correction for the peak fitting was carried out by the Shirley method using Kratos software preinstalled with the ESCA-3200. The W 4f spectra were deconvoluted using the area ratios of 1.33 [9] for a spin–orbit splitting of 2.1 eV. The atomic ratios were determined using the sensitivity factors provided by the manufacturer.

2.3. Electrochemical measurements

The voltammetric measurements were performed using an RDE (HZ-5000, Hokuto Denko) apparatus composed of a platinum counter, a standard calomel reference (SCE), and the phosphides on a glassy-carbon disk as the working electrode. Fifty mg of the catalyst was well dispersed in a 35% ethanol solution (1 mL) and then sonicated to form a 0.05 cat.-g mL^{-1} solution. Ten μL of the ethanol-catalyst solution was then dropped onto the glassy-carbon disk. After the catalyst was applied to the disk at 26 μg cm^{-1} (5 μg based on the electrode area), a 5-μL aliquot of a 5 wt% 2-propanol solution containing Nafion (Aldrich) was dropped onto the glassy-carbon disk. The RDE attached to a three-compartment electrochemical cell was placed in a 0.5 M H_2SO_4 solution. The measurement was carried out at room temperature and a rotation speed of 2000 rpm at 50 mV s^{-1} for the cyclic voltammetry (CV) and at 5 mV s^{-1} for the slow scan voltammetry (SSV) with scans from −0.2 to 1.0 V to determine the current density in Ar and H_2 (21.8 mL min^{-1}). The scanning was carried out several times to obtain the steady state values. The current densities were obtained from the current normalized to the sample's geometric area (0.196 cm^2) and with the current normalized to the electrode BET area. All the potential values in this measurement are obtained with respect to the SCE unless specified.

3. Results and discussion

3.1. TPR

The evolution of water during the TPR of MoP, WP, CoP, Co–WP and Co–MoP is presented in Fig. 1. The maximum evolution of water for CoP was at 823 K, while that for the WP and MoP was between 923 and 973 K. However, the maximum for the bimetallic Co–WP and Co–MoP was around 873 K, which was lower than that for WP and higher than those for NiP and CoP. Since Clark et al. [10] reported that the high surface area and CO uptake follow the trends of the water evolution profiles; therefore, the final temperatures in the present study as listed in Table 1 were determined by the highest evolution of water during the TPR. Although Stinner et al. [11] synthesized binary phosphides (Co–MoP) at 1023 K, the present study by TPR showed that Co–MoP is also formed at 873 K; thus high temperature is not necessary for the preparation. The addition of Co or Ni probably enhanced the phosphidation probably by assisting the dissociation of hydrogen and lowered the reduction temperature for phosphidation. Furthermore, in a previous paper, the low phosphidation temperature of Ni–MoP has shown to result in a higher catalytic activity for HDS than those of higher temperature [12].

3.2. XRD and physical properties

The XRD patterns of the WP, NiP and Ni–WP metal phosphides are shown in Fig. 2a, and those of WP, CoP and Co–WP are shown in Fig. 2b. The WP showed peaks at 2θ = 21.0°, 28.6°, 31.0°, 43.1°, 44.5° and 46.4° that perfectly matched the reference. The peaks of NiP and CoP corresponded well to dinickel phosphide and dicobalt phosphide. The NiP crystallites undergo simultaneous crystallization because the preparation temperature for NiP is the lowest (823 K) compared to the other phosphide catalysts. This conclusion was corroborated in the thermokinetic studies by Budniok and Matyja [13]. Ni–WP showed XRD peaks that are difficult to assign because of the presence of WP and NiP. However, in this study, three peaks at 2θ = 35.2°, 39.8° and 43.8° were observed. The main peak shifted to 39.8° and another peak appeared at 2θ = 35.1° due to the formation of the NiW bimetallic phosphide.

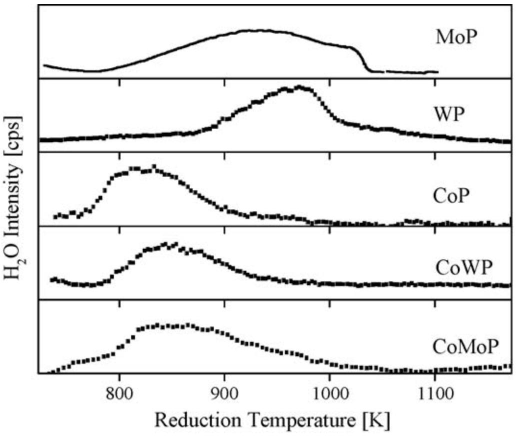

Fig. 1. The evolution of H_2O (m/z = 18) during temperature-programmed reduction in hydrogen gas measured using an online mass spectrometer for MoP, WP, CoP, Co–WP and Co–MoP.