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Pt–Ir binary hydrophobic catalysts: Effects of Ir content and particle size on catalytic performance for liquid phase catalytic exchange

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ABSTRACT

Pt/C and Pt–Ir/C catalysts with different atomic ratios were synthesized in a closed PTFE vessel by a microwave-irradiated polyol method. The characterization results indicated that the average Pt–Ir particle size changed only slightly and the face-centered crystalline structure gradually became more amorphous with increasing iridium content. The particle size could be controlled by altering the pH of the synthesis solution and the microwave heating rate. The carbon-supported catalysts and polytetrafluoroethylene were then loaded together on a foamed nickel (FN) carrier to obtain hydrophobic catalysts. The reaction mechanisms were presented for liquid phase catalytic exchange reaction, which could explain that a hydrophobic catalyst with a Pt/Ir molar ratio of 4/1 exhibited the best catalytic activity. Furthermore, the effect of particle size on catalytic performance was investigated. The activity of the Pt₄Ir₁/C/FN catalyst was enhanced by decreasing the average particle size, in the range of 2.5–3.8 nm.

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1. Introduction

Liquid phase catalytic exchange (LPCE) between liquid water and gaseous hydrogen is an important reaction for separation of the hydrogen isotope from liquid water. It usually occurs in the range between ambient temperature and 353 K. Accordingly, LPCE has some advantages, such as energy savings and high safety, in comparison with vapor phase catalytic exchange (VPCE) reactions, which occur above 473 K [1]. More importantly, it has much higher equilibrium separation factors than the VPCE [1] because the equilibrium separation factor for the hydrogen isotopic exchange reaction drops significantly with increasing reaction temperature.

Liquid water will block up the reaction channels and cover the active metallic clusters in conventional hydrophilic catalysts for LPCE, such as metallic oxide supported noble metal catalysts [2–5], causing strong mass-transfer limitations and catalyst “poisoning”. In 1972, Stevens published the first patent for a hydrophobic catalyst for LPCE at low temperature [2]. A waterproofing property of Stevens’s catalyst prevents liquid water from entering the catalyst micropores. Therefore, the LPCE can be carried out successfully. After several decades of development, three types of hydrophobic catalyst are now mainly used in the LPCE processes, including a Pt/C/inert carrier (Pt/C/IC) [3,4], Pt/C/polytetrafluoroethylene (Pt/C/PTFE) [5–9] and a Pt/styrene divinylbenzene copolymer (Pt/SDB) [10–12]. A simple fabrication method for the hydrophobic Pt/C/IC

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catalyst is as follows. Pt/C and PTFE are loaded together on an inert carrier to obtain a hydrophobic catalyst and the PTFE is utilized for waterproofing the catalyst and binding the Pt/C with the IC. The carbon substrate can be used for fabricating a highly dispersed metal based catalyst and the PTFE easily forms a good hydrophobic environment. Thus, this kind of hydrophobic catalyst is considered to have a good potential for development. The properties of the IC influence the catalytic activity and stability of the hydrophobic catalyst. Ceramic materials and stainless steel screens have been mainly utilized as inert substrates until now [3,4]. Ceramic materials have good molding properties but their Pt loading capacity is very low because they have a small outer surface area. Stainless steel screens have a large outer surface area but their slippery surfaces require a special oxidation treatment to strengthen binding with the Pt/C. In the current research, a porous foamed nickel (FN) material, which has a coarse surface and a large surface area, was utilized as the inert substrate for the hydrophobic catalyst.

Platinum is now widely accepted as the most active metal at high and low temperatures and at other conditions used for hydrogen isotope exchange, compared with other metals used as catalysts [3]. Single platinum catalysts with a high cost are the most frequently reported for LPCE processes, and hence the development of hydrophobic catalysts for LPCE with high activity and low cost has been an important objective. Therefore, researchers have explored either non-Pt catalysts or Pt-based catalysts containing Pt at a reducing loading in combination with other metals. Several hydrophobic non-Pt catalysts, such as Ni, Ni–Cr, Ni–Sn, Ni–Pd and Ni–Cr–Pd, have been prepared [3]. However, their catalytic activities are too low to be practical compared with Pt-based catalysts. The catalytic performance of Pt catalysts can be improved by appropriate addition of Cr or Ti [3]. Moreover, Pt–Ti catalysts show good stability in a water medium [3]. It was also reported [13] that the hydrophobic Pt–Ir bimetallic catalyst has a higher activity than pure Pt. However, the reason of the increasing activity was not analyzed in depth.

Another major approach to improving the activity of Pt-based hydrophobic catalysts is to optimize the synthesis procedure of carbon-supported catalysts, which determines the particle size and other microstructural characteristics of the active metal. It is well known that a small particle size will provide a large interface at which the reaction happens. Therefore, catalytic performance usually increases with increasing dispersion of the active metal for most reactions and catalysts. By controlling the Pt particle size and studying the relationship between Pt particle size and catalytic performance, an optimal particle size for the hydrophobic catalyst will be obtained for LPCE. Our group [14] reported that a hydrophobic catalyst with the smallest Pt particle size had the highest catalytic performance and described the preparation of Pt/C catalysts with an average particle size ranging from 1.8 to 3.5 nm, using a modified impregnation–reduction method. However, an optimal particle size range also exists for some reactions and catalysts [15,16]. To the authors' knowledge, there are no published reports about the effect of particle size for Pt-based binary catalysts for LPCE.

The aim of this work was to improve the performance of Pt-based hydrophobic catalysts by appropriate addition of the

element Ir and the optimization of the fabrication method for Pt–Ir/C catalysts. First, Pt–Ir/C catalysts having different ratios of Pt to Ir were prepared by a modified microwave-irradiated polyol method, and methods for control of the mean particle size were studied. PTFE was then used for waterproofing the catalyst and hydrophobic Pt–Ir/C/FN catalysts were fabricated. Finally, the effects of the Pt/Ir molar ratio and particle size on the catalytic activity for LPCE were investigated and discussed.

2. Experimental

2.1. Preparation of Pt/C and Pt–Ir/C catalysts

Pt–Ir/C catalysts were prepared by a modified microwave-irradiated polyol process. The carbon support used was Vulcan XC-72R ($S_{\text{BET}} = 230 \text{ m}^2/\text{g}$, Carbot Corp.) carbon black. Hexahydrated chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and hexahydrated chloroiridic acid ($\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$) were used as the precursors for the Pt–Ir catalyst. In a typical process, a Pt–Ir/C catalyst with a Pt/Ir molar ratio of 4/1 was prepared as follows. Appropriate amounts of Vulcan XC-72R (400 mg), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (212.4 mg) and $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ (53.6 mg) were added to 40 mL of ethylene glycol (EG) under ultrasonic stirring. The pH of the synthesis solution was adjusted using a 1 mol/L NaOH solution of EG. The synthesis reaction was performed in a closed PTFE vessel using an ETHOS T microwave labstation (2450 MHz, 1000 W, Milestone Corp.). The synthesis solution was heated to 463 K at a controlled rate by microwave heating and then kept at 463 K for 30 min. The highest synthesis pressure was about 2 MPa. After cooling to ambient temperature, the resulting powder catalyst was filtered and washed with abundant deionized water. The resulting $\text{Pt}_4\text{Ir}_1/\text{C}$ catalyst was dried in an oven at 378 K for 4 h. For comparison, a Pt/C catalyst was synthesized by the same method. The total content of Pt and Ir was maintained at 20 wt% in all of the carbon-supported catalysts. Nomenclature for the catalyst samples was of the following form: $\text{Pt}_4\text{Ir}_1/\text{C}$ –HR140–pH11.0, i.e. a catalyst with a Pt/Ir molar ratio of 4/1 was prepared at a heating rate of 140 K/min at pH 11.0.

2.2. Physical characterization of the Pt/C and Pt–Ir/C catalysts

The crystallinities of the Pt/C and Pt–Ir/C catalyst samples were examined by powder X-ray Diffraction (XRD) on a DX-2600 SSC diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5405 \text{ \AA}$) at a scanning rate of $1.2^\circ/\text{min}$ from 10° to 90° . The Scherrer and Bragg formulae were employed to calculate the mean diameter and the lattice parameter of the catalysts. The morphology and dispersion of the catalysts were determined on a JEOL JEM 3010 transmission electron microscope (TEM), using an acceleration voltage of 300 kV. The chemical composition analyses were performed with an EDAX Genesis 60S energy dispersive X-ray (EDX) detector, combined with an LEO S440 scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) analyses were carried out on an ESCA lab 250 spectrometer. Narrow scan photoelectron spectra of Pt 4f and Ir 4f were recorded and deconvoluted by XPSPEAK (version 4.1).

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