Pt–Co bimetallic catalyst supported on single walled carbon nanotube: XAS and aqueous phase reforming activity studies

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ABSTRACT

We have developed a simple method to create a catalyst with atomically dispersed Pt on top of Co nanoparticles on single walled carbon nanotubes (SWNT) supports by sequential impregnation of Pt(II) and Co(II) solutions following by hydrogen reduction. The aqueous phase reforming activity is much higher than for Pt monometallic catalysts on SWNT supports prepared by several methods, either pre-reduced in hydrogen or in the liquid phase. The high selectivity of the monometallic catalysts is maintained for the bimetallic systems. The Extended X-ray Absorption Fine Structure (EXAFS) results at the Pt L_{III} edge show no observable Pt–Pt bond. Only Pt–Co bonds were observed, indicating high dispersion of Pt. The enhanced activity comes from two sources: the high dispersion of Pt and the effect of the Co as co-catalyst or modifier. This contribution demonstrates the possibility to further engineer bimetallic catalysts to improve the aqueous phase reforming activity, especially to retain good selectivity at high conversion.

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1. Introduction

Hydrogen fuel cells are promising devices for clean and efficient energy for a variety of applications [1]. The current hydrogen production method, the steam reforming of hydrocarbons from fossil fuels, however, is not environmentally friendly. In addition, the carbon monoxide (CO) impurity in the hydrogen stream from the steam reforming products causes poisoning of the fuel cell anode catalyst [2].

Dumesic and co-workers have developed an aqueous phase reforming (APR) process which uses an oxide (alumina or silica) supported Pt catalyst to catalyze the reforming of oxygenated hydrocarbons in aqueous solution at relatively low temperature (200–250 °C), to produce hydrogen and carbon dioxide (CO_2) with a low level of CO [3]. The reaction can be stoichiometrically written as (taking ethylene glycol for example):

$$C_2H_6O_2 + 2H_2O \rightarrow 5H_2 + 2CO_2$$
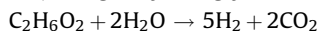
However, the oxide supports are not very stable in the aqueous phase at these reaction conditions. Therefore, less reactive or inert catalyst supports are desired for APR. Recently we have decorated Pt nanoparticles on single walled carbon nanotubes (SWNT) using a wet-reduction method, and this Pt–SWNT catalyst showed

higher APR activity than the alumina supported catalyst. In addition, the catalytic activity and selectivity remained unchanged after a week of steady-state reaction. We also developed a Pt–Co bimetallic catalyst supported on SWNT by separately decorating Pt and Co nanoparticles on SWNT. This Pt–Co on SWNT catalyst increased the APR activity five fold compared with the Pt–SWNT catalyst from the wet-reduction method. The Extended X-ray Absorption Fine Structure (EXAFS) results indicated the co-existence of Pt and Co nanoparticles with no Pt–Co bimetallic phase [4].

Huber et al. also showed that adding Co to a Pt/alumina catalyst significantly increased the activity of the catalyst [5]. They used an incipient wetness impregnation method for both Pt and Co, thus their catalyst is more likely to have bimetallic Pt–Co nano-alloy particles than individual Pt and Co nanoparticles, but no detailed research has been carried out to understand the structure of the metal species on the sequentially impregnated Pt–Co bimetallic APR catalyst.

In this work, we prepared the Pt–Co/SWNT catalyst using an incipient wetness impregnation method and tested its APR activity. Shabaker et al. have compared a variety of supports for Pt APR [6] that included activated carbon, which had comparable activity to an alumina support. Different temperature and pressure of reaction prohibit a direct comparison with the SWNT activity reported in this work. APR reaction was also performed on Pt/SWNT catalyst prepared by a similar incipient wetness impregnation method and Pt–SWNT catalyst prepared by a wet-reduction

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method for comparison. In-situ X-ray absorption spectroscopy (XAS) was utilized to obtain the structure and oxidation state information on the catalysts and to explore the structure–activity relationship.

The Pt–Co bimetallic system can stoichiometrically form PtCo, $PtCo_3$, and Pt_3Co alloy phases, with both crystalline (ordered) and amorphous (disordered) structures [7], and at mild temperatures as used in this work, it is likely to form an amorphous random alloy [8]. A detailed X-ray Absorption Near Edge Structure (XANES) study also indicated that the formation of a Pt–Co alloy phase would cause electron transfer between these two elements, which leads to the change of white line intensity and other near edge characteristic peaks [9]. However, these previous experiments were all performed on bulk phase Pt–Co alloys, not extending to nano-alloys. Recently Pt–Co bimetallic nanoparticles have been developed for catalysis [10,11], electrochemistry [12,13] and supermagnetic recording materials [14,15]. XAS analysis has been done [10,11] on Pt–Co bimetallic catalysts impregnated on alumina or zeolite supports with Pt as the minor component of the bimetallic system. However, they all conclude that from XAS, they can observe Pt–Co bonding at the Pt L_{III} edge, but cannot see Co–Pt bonding at the Co K edge, which is not consistent with mass conservation. In this paper we would like to present a detailed XAS spectral analysis to further explore the Pt–Co bimetallic structure in a nano-alloyed particle supported on carbon nanotubes.

2. Experimental

2.1. Catalyst synthesis

The SWNT used in this research was purchased from Cheap Tubes Inc., and labeled as cSWNT. The surface area of the cSWNT is 407 m^2/g and the pore volume is 2 cm^3/g. The carbon nanotubes were refluxed with 2.6 M nitric acid overnight, filtered and dried for further use.

The Pt on SWNT catalyst was prepared by incipient wetness impregnation. Tetra-ammine platinum(II) nitrate (from Strem Chemicals) was dissolved in water and the solution was added to the nitric acid treated SWNT dropwise until incipient wetness. The catalyst was labeled as Pt/cSWNT, and the loading of Pt was 8.0 wt%, which is confirmed by the edge jump of X-ray absorption [16]. The Pt–Co bimetallic catalyst was prepared by a sequential impregnation method. Pt/cSWNT was prepared as stated above and dried at 60 °C over night, and then cobalt(II) nitrate (from Sigma–Aldrich) solution was added to the already-prepared Pt/cSWNT dropwise until incipient wetness. Equal weights of Pt and Co were used, thus the molar ratio of Pt to Co is 0.30. Both Pt/cSWNT and Pt–Co/cSWNT were air dried at 150 °C before use.

The wet-reduction method has been described elsewhere [17] and applied to our lab-made SWNT [4] before. Potassium

tetrachloroplatinate(II) (from Sigma–Aldrich) was dissolved in ethylene glycol–water mixture with nitric acid treated cSWNT and refluxed for 8 h. The product was filtered, dried and labeled Pt–cSWNT–EG.

2.2. Activity test

The APR activity test was carried out in a fixed bed reactor followed by a condenser and a gas–liquid separator, and the design is reported elsewhere [5]. Fifty milligrams of catalyst was placed in the reactor and 10 wt% ethylene glycol aqueous solution was introduced into the reactor at 60 μL/min via an HPLC pump. The reaction was carried out at 225 °C and 380 psig, and the gas products were analyzed by an online Varian CP-3800 gas chromatography.

2.3. Structural analysis

X-ray absorption experiments were carried out at beamline X18B at NSLS, Brookhaven National Lab. Around 30 mg of the catalyst was well mixed with 270 mg boron nitride power by grinding, and then pressed into a self supporting pellet which was then placed in a stainless steel in-situ reaction cell. Data were collected at both the Co K edge (7709 eV) and the Pt L_{III} edge (11564 eV) in transmission mode, and a corresponding metal foil was used as an internal reference. The catalysts were reduced in-situ in flowing hydrogen, and the temperature was first ramped up to 400 °C in 20 min, and then held for 30 min. Time-resolved XANES spectra were measured throughout this procedure. After reduction, the system was cooled to room temperature in flowing hydrogen by liquid nitrogen. Extended X-ray absorption fine structure was measured before and after reduction, both at room temperature. The EXAFS data was analyzed and fitted using the IFEFFIT 1.2.10 software package [18].

3. Results and discussion

3.1. APR activity results

The catalyst activity and selectivity data for both monometallic and bimetallic catalyst systems supported on cSWNT supports are shown in Table 1. Among the monometallic catalysts, the Pt–cSWNT–EG catalyst prepared from the wet-reduction method shows higher activity than the Pt/cSWNT catalyst prepared from the incipient wetness impregnation method, with the latter showing almost no hydrogen production. However, the Pt–Co/cSWNT catalyst prepared from the sequential impregnation method shows 3 times higher activity than the Pt–cSWNT–EG catalyst, while the selectivity is not much affected. Some of the reactivity data from the literature are also compared here, from

Table 1
The aqueous phase reforming reactivity of different Pt and Pt–Co catalyst supported on different SWNT supports.

Catalyst	Pre-reduction	Catalyst mass time yield[a]	Pt mass time yield[b]	Conversion[c]	Hydrogen selectivity[d]	Alkane selectivity[e]
Pt–cSWNT–EG	No	0.51	6.5	4.5%	92%	12.6%
Pt/cSWNT	Yes	N/A[f]	N/A[f]	0.4%	N/A[f]	11.7%
Pt–Co/cSWNT	Yes	1.78	24.7	16.5%	~100%	7.1%
Pt/Al$_2$O$_3$[g]	Yes	0.45	15	5.4%	87%	1.2%
Pt–Co/Al$_2$O$_3$[g]	Yes	0.69	23	8.4%	88%	0.5%

[a] Measured by millimole hydrogen per gram catalyst per minute.
[b] Measured by millimole hydrogen per gram platinum in the catalyst per minute.
[c] Evaluated by CO_2 production with respect to the ethylene glycol feed.
[d] Calculated as (molecules H_2 produced/C atoms in gas phase)(2/5).
[e] Calculated as (C atoms in gaseous alkanes)/(total C atoms in gas-phase product).
[f] The hydrogen yield for this catalyst is below the detection limit.
[g] Reference data from Huber et al. [5].