Support Effect on the Dispersion and Aqueous Phase Reforming Activity of Carbon Nanotube Supported Platinum Catalysts

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Introduction

Heterogeneous catalysts in industrial use are generally comprised of a metal or oxide active component on a high surface area support, which is typically an oxide. Carbon, as a catalyst support, has drawn our attention recently, basically for two reasons. First, carbon nanotubes, a new form of high surface area carbon, have recently been discovered and used as a heterogeneous catalyst support. [1] Second, carbon supports are resistant to dissolution in high temperature aqueous solution, which is important for the production of hydrogen via aqueous phase reforming of biomass derivatives. [2]

In this study, multi-walled carbon nanotube (MWNT) supported Pt catalysts were prepared and applied in aqueous phase reforming of ethylene glycol. The effect of Pt precursor, carbon surface chemistry, MWNT diameter and porosity has been studied, and correlated with the dispersion of Pt nanoparticles on MWNT, and the activity in aqueous phase reforming (APR).

Materials and Methods

MWNT was purchased from Cheap Tubes, Inc. Pt/MWNT catalysts were prepared by incipient wetness impregnation of tetra-ammine platinum (II) nitrate (from Aldrich) with 8 wt% loading. The MWNT supports were characterized by nitrogen physisorption, near edge X-ray absorption fine structure (NEXAFS), X-ray diffraction (XRD), and Raman spectra, and the catalysts were studied using transmission electron microscopy (TEM), extended X-ray absorption fine structure (EXAFS). The APR reactor was constructed according to the literature. [3] The catalysts were pre-reduced in hydrogen at 400°C, and then reacted with 10 wt% ethylene glycol solution at 225°C.

Results and Discussion

In order to study the effect of carbon surface chemistry, MWNT with different surface functional groups were prepared. The as-received MWNT was refluxed with nitric acid to open the tube ends. The HNO_3 treatment also introduced some oxygen containing groups, including carboxylic, phenol and/or quinone groups. Further high temperature (1000°C) treatment was applied after the HNO_3 treatment. These three MWNTs were labeled MWNT-r, MWNT-n and MWNT-ht, respectively. Nitrogen physisorption results indicated that MWNT-r has no ordered pores, while both MWNT-n and MWNT-ht shows a narrow pore size distribution around 3.8 nm, which is verified by TEM to be the MWNT inner diameter. The effectiveness of oxygen removal is verified by NEXAFS in Figure 1. The peaks at 288 and 290 eV are assigned to C-O and C=O bonds, respectively. Thus after high temperature treatment, most of the oxygen was removed, while the nanotube remained open-ended.

The dispersion of these catalysts was measured by EXAFS and TEM, and indicated that Pt/MWNT-n gives the highest dispersion. This is attributed to the ionic interaction between the support and the Pt precursor. Since the Pt precursor is a cation, it interacts strongly with negatively charged groups, such as carboxylic groups, thus the Pt tends not to aggregate. A comparison also shows anion Pt precursor gives much larger Pt particles. The APR activity is also related to the surface functionality. Table 1 show that Pt/MWNT-n, although having the best dispersion, gives the lowest yield and turnover frequency (TOF). It has been suggested that the oxygen containing groups may sterically prevent the reactant from making contact with the catalyst particles. [4]

While functionalization is necessary to get high dispersion, interaction of the small particles with oxygen anchors lowers the reactivity. Using different combinations of thermal and chemical reduction of the nitric acid treated MWNT-n support can be used to optimize the density of C-O-H functional groups which to give improved dispersion with little deactivation of the resulting small Pt particles. These are on-going experiments and will be discussed.

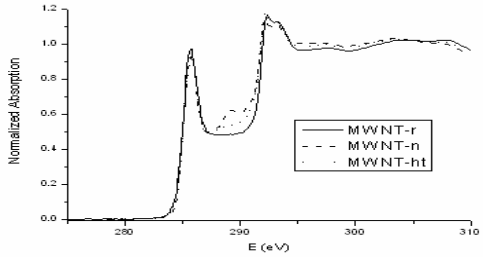

Figure 1. Carbon edge NEXAFS spectra of MWNT with different surface chemistry.

Table 1. APR activity of Pt/MWNT catalyst with different surface chemistry.

Catalyst	Oxygen Content	Particle Size (nm) (EXAFS/TEM)	Pt Mass Time Yield (mmol H_2/(g Pt*min))	Turnover Frequency (min^{-1})
Pt/MWNT-r	N/A	2.15/2.29	12.3	3.72
Pt/MWNT-n	8.86%	1.07/1.09	11.6	1.75
Pt/MWNT-ht	1.82%	1.32/1.21	19.0	3.53

Significance

This paper systematically studied different effects on the dispersion and APR activity of Pt supported on MWNT. The results could be useful for the study of other carbon supported aqueous phase heterogeneous catalysis.

References

1. Lordi, V., Yao, N., Wei, J., *Chem. Mater.*13, 733 (2001).
2. Cortright, R.D., Davda, R.R., Dumesic, J.A.,*Nature* 418, 964 (2002)
3. Huber, G.W., Shabaker, J.W., Evans, S.T., Dumesic, J.A., *Appl. Catal. B Env.* 62, 226 (2006).
4. Toebes, M.L., Zhang, Y.H., Hajek, J., Nijhuis, T.A., Bitter, J.H., van Dillen, A.J., Murzin, D.Y., Koningsberger, D.C., de Jong, K.P., *J. Catal.* 226, 215 (2004).