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CNFs-supported Pt catalyst for hydrogen evolution from decalin

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ABSTRACT

Carbon nanofibers (CNFs) with different microstructures were synthesized as the support of Pt catalyst for decalin dehydrogenation to evolve pure hydrogen. The results show that in a liquid-film state at the temperature of 240 °C for reactor external heating, 5 wt% Pt catalyst supported on platelet CNFs gives a TOF of 732.4 mol H_2/mol metal in 2 h. The microstructure of CNFs and the metal particle size have great impact on the performance of the catalyst for the reaction.

1. Introduction

Cyclic-hydrocarbons such as decalin and cyclohexane that have ample hydrogen contents are promising hydrogen carriers. Meanwhile, there is no CO and CO_2 releasing during the reversible dehydrogenation–hydrogenation of the cyclic-hydrocarbon reaction pairs [1–3]. Supported precious metal catalysts have been reported to be active for the dehydrogenation of cyclic-hydrocarbons and activated carbon is the most commonly used support material in the literature [4,5]. The concepts of "liquid-film state" and "wet–dry condition" have been developed to overcome the thermodynamic equilibrium limitation, thus to achieve higher reaction conversions at mild reaction conditions. However, more efficient catalytic system and consequently much higher hydrogen evolution rate are desired in order to meet the demand of hydrogen supply for fuel cells and applications in energy storage.

Carbon nanofibers (CNFs) have aroused extensive interests especially in catalysis field owing to their unique physico-chemical properties. The outstanding advantages of CNFs as catalyst support compared with activated carbon lay mainly in three aspects [6–8]. First, it is possible to tailor the microstructures of CNFs by properly selecting growing techniques and to control the surface chemistry of CNFs by surface modification. Second, the almost completely exposed surface of the CNFs may relieve the resistance of inner pore diffusion. Third, the presence of specific metal-support interactions may enhance the catalytic activity and the selectivity. CNFs have frequently been employed as catalyst supports for selective hydrogenation [7,9] and dehydrogenation [10], or as electro-catalytic materials for fuel cells [8,11]. For decalin dehydrogenation, however, little attention has been paid to the use of CNFs support [12,13].

In the present work, CNFs have been adopted as the support of Pt catalyst for decalin dehydrogenation, and the effects of the microstructure of CNFs and the metal loading on the performance of Pt/CNFs catalyst have been investigated. The purpose of the study is to take advantage of the peculiar features of CNFs to prepare high efficient supported Pt catalysts.

2. Experimental

CNFs with tube, fishbone, and platelet types of microstructure were synthesized by CVD method using CO as carbon source and Ni/γ-Al_2O_3, NiFe/γ-Al_2O_3 and nano-particles of Fe, respectively, as the catalysts [14]. The synthesis procedures were the same as that described in Ref. [15] excepting the catalyst composition used. The CNFs as synthesized were then purified by turns with 4 M NaOH and 4 M HCl aqueous solution, each lasting for 2 h at 60 °C under vigorous agitation to remove γ-Al_2O_3 and the metals, respectively. After repeating this purification procedure twice, the residues in the CNFs contained less than 0.3 wt% Al_2O_3 and 0.1 wt% Ni and Fe, as detected by ICP technique (Optima 2100 DV, PerkinElmer Instruments). To modify the surface characteristics of the CNFs, they were immersed in concentrated H_2O_2 solution for 24 h at ambient temperature or placed in static air at 400 °C for 6 h. On the purified CNFs with different microstructures, Pt nanoparticles

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were supported by colloid method in which ethylene glycol was used as a reductant [16]. For comparison, a commercial carbon support XC-72 (Johnson Matthey) was also used to support Pt. In addition, incipient wetness impregnation method was used to prepare Pd/CNFs catalyst [17] for comparison. The TPD-MS profiles of the CNFs were detected by Micromeretics Autochem II and Quester GP (ABB Automation Inc.). The metal particles on the surface of CNFs were observed by HRTEM (JEOL JEM-2100). Their dispersion was determined by using CO as adsorbate.

Dehydrogenation of decalin to naphthalene was carried out under atmospheric pressure in a 100 ml Erlenmeyer flask which was mounted with a reflux condenser and was placed on a plate heater regulated at 240 °C. Under a typical reaction condition, i.e., 0.2 g catalyst powder, 2 ml decalin feed and 2 h reaction time, the temperature inside the reactor was spontaneously maintained at 193 °C during the reaction after reaching the equilibrium of liquid evaporation and condensation. The hydrogen evolved from the reactor during reaction and the residual liquid in the reactor after reaction were analyzed by GC (HP 6890) using TCD and FID, respectively. The products in the liquid were detected to be tetralin and naphthalene. The evolved hydrogen was monitored by a soap bubble flow meter, and the mass of the liquid was weighed before and after the reaction to determine carbon mass balance. The carbon mass loss was found within 4 wt%, which was mainly due to the escape of the vapor. The conversion of the decalin was defined as the ratio of mass change of decalin before and after the reaction to the mass of decalin added to the reactor before the reaction, and the selectivity to naphthalene was the ratio of the naphthalene among the products. The value of TOF was calculated as the accumulative moles of hydrogen derived from decalin selective conversion on per mol metal divided by the elapsed time for reaction.

3. Results and discussion

3.1. Effect of microstructure and surface modification of CNFs

The CNFs with tube (t-CNFs), fishbone (f-CNFs), and platelet (p-CNFs), microstructures are, respectively, shown in Fig. 1a–c. It is clear that the individual CNF consists of graphene sheets aligned in a definite direction to the fiber axis [8,18]. The results of catalytic dehydrogenation of decalin over 1 wt% Pt/CNFs and 5 wt% Pt/CNFs with different support microstructures are listed in Table 1, which are compared with the tests over 1 wt% Pt/XC-72 and 5 wt% Pd/p-CNFs.

It can be found that the platelet CNFs (p-CNFs) are the most effective support for Pt catalyst among the three structural types of CNFs and XC-72 in terms of TOF obtained, while the tubular CNFs are least effective. As displayed in Fig. 1, the surface of the tube CNF behaves basal graphene sheets that are parallel to the fiber axis. In contrast, exposing on the surface of the platelet CNFs are the edges of stacked graphene sheets that are perpendicular to the fiber axis. As for XC-72, it is an amorphous carbon consisting of fused particles in a chain-like structure [8]. Because of the inherent differences in geometric and electronic micro-environments of the supports [19,20], the anchorages of the metal particles are different on different carbon support surfaces. The metal particle size and the metal-support interaction on different supported Pt catalysts are therefore distinguishing, resulting in different catalytic performances [8,11].

Table 1
Results of dehydrogenation of decalin over Pt/CNFs with different microstructures.

Catalyst	Conversion (%)	Selectivity (%)	TOF (mol H_2/mol metal)
1 wt% Pt/XC-72	5.32	58.62	359.9
1 wt% Pt/t-CNFs	0.71	24.05	40.0
1 wt% Pt/f-CNFs	4.62	73.73	335.3
1 wt% Pt/p-CNFs	6.89	70.56	491.2
5 wt% Pt/t-CNFs	23.51	84.70	357.0
5 wt% Pt/f-CNFs	39.63	92.24	620.4
5 wt% Pt/p-CNFs	46.32	93.19	732.4
5 wt% Pd/p-CNFs	4.32	95.52	58.6
5 wt% Pd/p-CNFs–H_2O_2	6.76	97.39	97.9
5 wt% Pd/p-CNFs–air	3.15	95.39	44.3

The Pt catalysts exhibit much higher activity than do the Pd catalyst but have slightly smaller selectivity. Oxidative surface treatment of p-CNFs has been conducted in order to improve the performance of the Pd/p-CNFs catalyst [7,21,22]. The results in Table 1 show that the Pd particles dispersed on the p-CNFs treated with H_2O_2 provide higher conversion and selectivity than those on either untreated or air-treated p-CNFs. TPD-MS profiles demonstrated in Fig. 2 reveal that p-CNFs-H_2O_2 produce more carboxyl and carboxylic anhydride groups [14,23]. On the contrary, more carbonyl and basic oxygenated groups are created on the surface of p-CNFs–air. Nevertheless, the TOF of 5 wt% Pd/p-CNFs–H_2O_2 is still far lower than those of 5 wt% Pt catalysts. Dispersion measurements of the Pt and Pd supported catalysts with 5 wt% metal loading indicate that the mean particle sizes of the Pt/p-CNFs, Pd/p-CNFs, Pd/p-CNFs–H_2O_2, and Pd/p-CNFs–air are 1.8, 2.1, 3.2 and 2.7 nm, respectively. The relatively larger particle size of Pd on the support may to some extent be responsible for the lower activity of Pd catalysts. Meanwhile, the strong absorption of hydrogen generally occurring on Pd metal may hold back the proceeding of dehydrogenation, resulting in inferior performance of Pd catalysts.

3.2. Effect of metal loading on catalytic performance of Pt/p-CNFs

As clearly shown in Table 2 that over the 5 wt% Pt/p-CNFs, both the conversion and the selectivity are the highest. Moreover, its TOF reaches 732.4 in 2 h, higher than 351.4 which was obtained under the comparable reaction condition over a 5 wt% Pt/C catalyst reported in the literature [24].

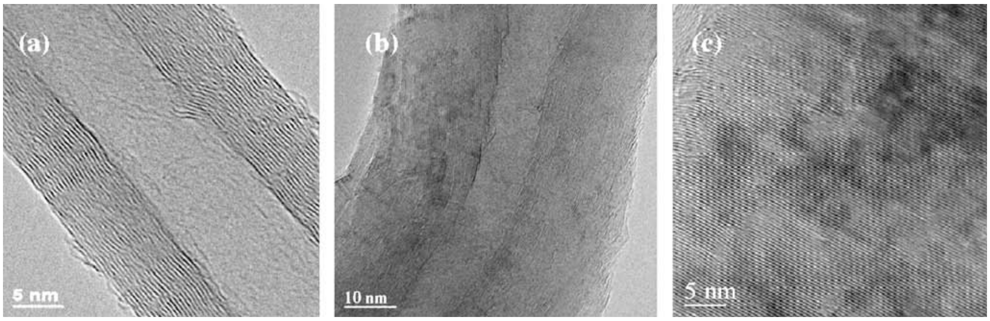

Fig. 1. HRTEM images of CNFs of three microstructures of: (a) tube; (b) fishbone; and (c) platelet.