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Catalysis Today 93–95 (2004) 347–352

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Palladium cluster filled in inner of carbon nanotubes and their catalytic properties in liquid phase benzene hydrogenation

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Abstract

This is the first report indicating the Pd clusters filled in multi-walled carbon nanotubes (MWNT) as catalyst applied in liquid phase benzene hydrogenation. The treatment of MWNT, filling of metals, the effects of the filling amount of palladium, evaluation of catalytic property, and the comparison with various conventional supports were investigated. The experiment results indicated that the Pd clusters filled in the inner of carbon nanotubes exhibited higher activity than other supports such as Y zeolite and activated carbon. According to various characterizations, the relationship between catalytic activity and the structure of the carrier was briefly discussed.

Keywords: Multi-walled carbon nanotube; Palladium; Liquid benzene hydrogenation

1. Introduction

Since the discovery of carbon nanotubes in 1991 [1], they have received an increasing interest both from a fundamental point of view and for potential industrial application [2–4]. These applications include their use as magnetic or sensor materials, for gas separation and storage, but the most promising seems to be as catalyst supports [5,6]. The carbon nanotubes exhibit exceptional properties such as uniform pore, higher H_2 uptake capacity [7], large specific surface area, and the hydrophobic character of surface. Furthermore the diameter of the carbon nanotube obtained falls in the order of 10^0–10^2 nm, and the inner diameter of MWNT is about several nanometers to 10 nm. Such pore diameter allows any reactants arrived at active centers, has enough space for the reaction and desorption of products. Those properties suggest enormous potential applications of carbon nanotubes as novel materials for the catalyst carrier. Some researchers reported that the catalysts metal supported on multi-walled carbon nanotubes exhibited much better activity than other carbon-based supports for some hydrogenation reactions. The structure of carbon nanotubes can display unusual behaviors compared to conventional supports, especially for liquid-phase reaction, in which diffusion of reactants into the solid matrix and back-diffusion of the products are significantly influenced by the external size of the particles [8].

However, so far all of the metal species reported were supported on the exterior of carbon nanotubes when use them as carrier of catalyst. It is interesting that how to use the capillary siphon action of nanotubes to filling the transition metals into the inside of carbon nanotubes on a large scale and use space effect of nanotubes to carry out catalytic reaction. Here we reported firstly filling of palladium clusters in the inner of carbon nanotubes successfully and evaluation for the performance of liquid phase benzene hydrogenation.

2. Experimental

2.1. Preparation of carbon nanotubes and Pd-MWNTs catalyst

The MWNTs were prepared by catalytic decomposition of acetylene at 700 °C. The catalysts were produced by sol–gel action of cobalt nitrate and lanthanum nitrate under certain condition and calcined at 700 °C for 4 h. Twelve grams of as-synthesized carbon nanotubes were suspended in 400 ml of concentrated nitric acid with vigorous stirring and refluxing at 60 °C for 6 h. After filtered, the sample was washed

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doi:10.1016/j.cattod.2004.06.122

and dried at 100 °C for 4 h. Then the samples were oxidized in static air at 773 K. The filling of metal palladium clusters in the carbon nanotubes was carried out as follows: 1.0 g of oxidized carbon nanotubes contacts with palladium salt solution by incipient wetness impregnation technique, the different samples with loading amount 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0 wt.% were obtained respectively. Then heated in helium gas at 623 K for 3 h and subsequently reduced in hydrogen gas at 623 K for 3 h. The finally obtained samples were closed in a vacuum container for avoiding oxidation of palladium particles. The compared samples of Pd/Y and Pd/AC were prepared by the same method in which zeolite Y was obtained by exchanging NaY-type zeolite (CBV100, $SiO_2/Al_2O_3 = 5.1$) into to NH_4Y with the aqueous solution of ammonium nitrate, and active carbon was furnished by Aldrich Chemical Company Inc.

2.2. *Characterization of samples*

The morphometrics of carbon nanotubes were observed with the JEM-200 CX transmission electronic microscope (TEM). The specimens for TEM were dispersed in aqueous solution containing 50% alcohol by ultrasonic treatment and then dropped onto holey grids. The morphometrics of carbon nanotubes-supported Pd were observed by the Hitachi S-4300 Scanning Electron Microscopy (SEM) and the acceleration voltage is 20 kV. The specific surface area was measured by the method of nitrogen physisorption at liquid nitrogen temperature using a Micrometritics ASAP 2000 apparatus. XRD patterns were taken with a D/MAX X-ray diffraction instrument by using Cu Kα in the voltage of 40 kV and current of 50 mA.

2.3. *Activity evaluation of liquid phase benzene hydrogenation*

Liquid phase hydrogenation of benzene was carried out in a stainless steel reactor of 130 ml. The hydrogen volume was measured by a mass flow meter of high pressure. The reactor was filled with reactants of 12 ml the ethanol solution contained 5.8 wt.% benzene, and 100 mg of catalyst suspended in ethanol solution of benzene. The reactor was washed by hydrogen gas for three times before every reaction. Then the hydrogen was drawn into reaction system up to achieve certain pressure, stirred vigorously by magnetic stirrer. The reaction temperature was controlled at 363 K and the pressure was 10.0 kgf/cm^2. After 3 h of reaction, begin taking sample to analysis by Varian CP-3380 gas chromatograph with capillary column. TOF values were calculated according to the following equation:

$$\mathrm{TOF} = \frac{V \times (d/M) \times C \times 6.02 \times 10^{23} \times S}{N \times t}$$

Here V is the volume of benzene used in the hydrogenation, d the density of benzene, M the molecular mass of benzene, C the benzene conversion, S the selectivity to cyclohexane, N the number of Ni atoms, t the reaction time, and 6.02×10^{23} the Avogadro's number. The unit of TOF is per second (s^{-1}).

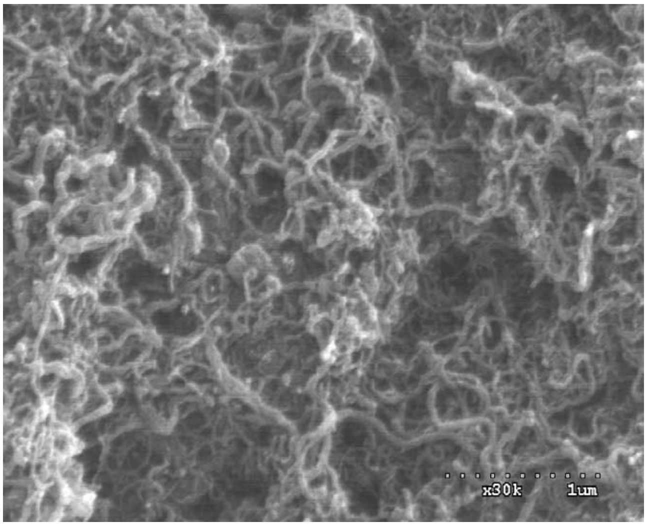


Fig. 1. SEM micrographs of as-synthetic multi-walled carbon nanotubes.

3. Results and discussion

3.1. *Treatment and opening of carbon nanotubes*

The SEM micrograph of as-prepared MWNTs is presented in Fig. 1. It can be seen that a mass of carbon nanotubes presented with random orientation. As shown in Fig. 2 the purified MWNT has an outer diameter of 30–50 nm, inner diameter of 5–10 nm, and lengths of mi-

Fig. 2. TEM micrographs of purified multi-walled carbon nanotubes.

Table 1
Specific surface areas of MWNTs after treatment under different conditions and that of compared supports

Treatment condition of MWNT	Specific surface areas (m^2/g)
As-synthetic MWNT	213.0
In nitric acid at 333 K for 6 h	224.4
In air at 573 K for 3 h	242.5
In vacuum at 823 K for 2 h	255.2
In mixed acid at 403 K for 10 h	263.0
In air at 823 K for 2 h	328.0
NaY	900.0
Active carbon	775.0

crometer range. According to the XRD patterns, all the purified carbon nanotubes exhibited only one sharp peak at $2\theta = 26.06^\circ$ between the range of $2\theta = 5^\circ$ and 50°, which indicated that the purified carbon nanotubes without other impurities have graphited-well structure. The specific surface area of as-prepared nanotubes is 213.0 m^2/g measured by nitrogen adsorption, and values of the acid-treatment nanotubes under different conditions are listed in Table 1.

The treatment of MWNTs is an important process for filling of metal palladium clusters since the end of the unprocessed carbon nanotubes is closed generally and their surface is hydrophobic. This process removed firstly the catalyst component and other impurities formed during synthesis. Then it can open the tip of carbon nanotube by etching away the closed nanotube to increase the specific surface. At the same time it can introduce a large number of functional groups on the surface of nanotubes. The process significantly influences the hydrophobic nature of carbon nanotubes and makes the surface more accessible to aqueous solution of metals. From Table 1 it can be seen that the specific surface areas increase to 224.4, 242.5 and 255.2 m^2/g after treatment with acid, oxidation, and vacuum respectively. And the value further increase to 263.0 and 328.0 m^2/g by treatment again with the mixed acid and air oxidation. The walls of the carbon nanotubes are constructed of concentric cylinders with spacing between the cylinders close to that of the interlayer spacing of 0.34 nm [9]. For the closed as-prepared MWNT, the measured surface area only indicates the outer surface of unprocessed MWNT. It is well known that the diameter of N_2 molecule is 0.454 nm, therefore the surface area increase after treatment under different conditions is attributed mainly to the inner wall of opened carbon nanotubes. We found that the increasing surface area by treatment with mixed acid and then oxidation in air is more than that by acid treatment. It may be resulted in that some tubes were peeled off by stronger mixed acid.

3.2. Palladium cluster dispersed in the inner of carbon nanotubes

Fig. 3 shows the TEM micrographs of Pd–MWNTs catalyst. It is clear that the spheroidal palladium clusters dispersed nicely in the inner of carbon nanotubes and are not on the exterior of nanotubes. The size of Pd metal clusters is in the range of 1–8 nm and the main diameter is in the range of 3–5 nm. An examination for the different amount of palladium suggests that the palladium clusters can be well dispersed in the inner of carbon nanotubes in the range of 2.0–12.0 wt.%.

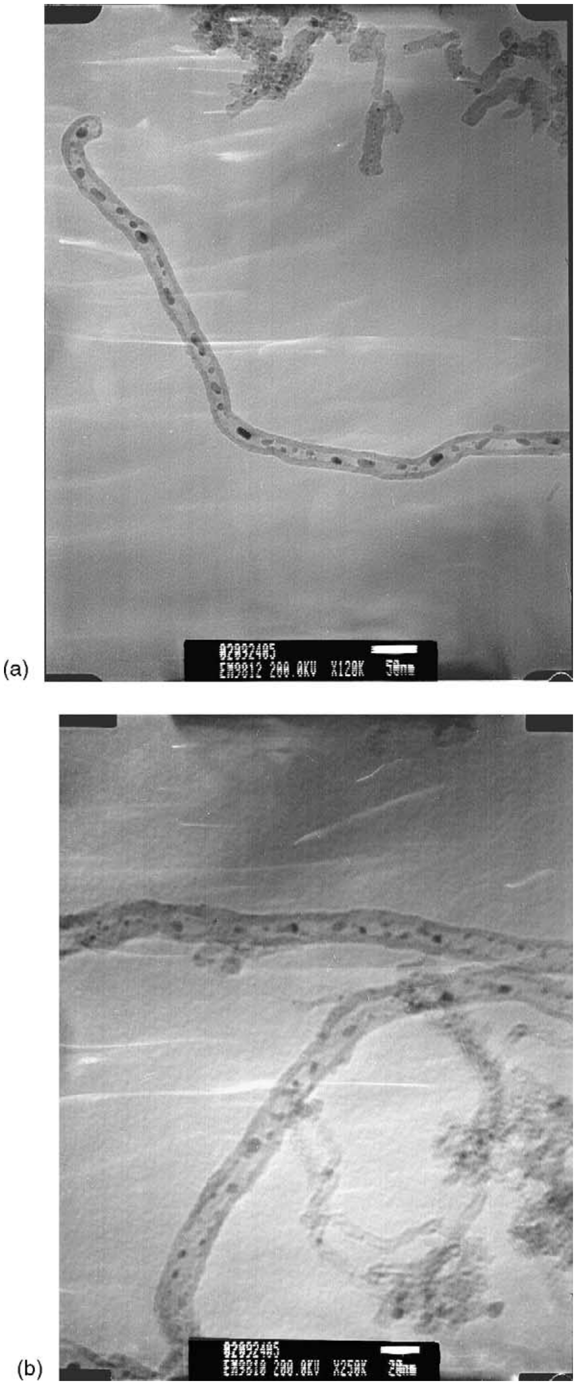
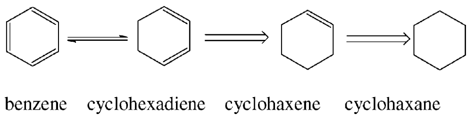


Fig. 3. (a) TEM micrographs of filled palladium clusters inside of carbon nanotubes. (b) TEM micrographs of filled palladium clusters inside of carbon nanotubes.

Carbon nanotubes constitute a novel class of nanomaterials with applications in catalysis and other areas [10,11]. Many researchers are interested in preparing decorated nanotubes by depositing metal clusters onto nanotube surfaces. However the efforts to deposit metal clusters directly on the surface of carbon nanotubes by various chemical means were not quite successful. And different methods of filling metals have been explored but in most cases, they work for a limited range of materials or in low yields of filling nanowire [12,13]. In order to obtain well-dispersed metal clusters with nanometric dimensions filled in the inner of carbon nanotubes, we have made use of pretreated surface of nanotubes and subsequent capillary action, resulted in to obtain the metal clusters well-dispersed in the inner of MWNTs. The phenomena of homogeneous dispersion can be attributed to a relatively strong metal–support interaction between the metal salt precursor and the graphite edges of the carbon nanotubes, owing to the resistance to the growth and aggregation of the small palladium particle. It has been observed in our laboratory that the size of palladium clusters was significantly modified depending on the inner diameter of carbon nanostructure, i.e. smaller clusters created in the smaller carbon nanotube and larger clusters created in the larger nanotube. For example, a sharp particle size distribution concentrated at around 5–7 nm of diameter in a larger inner diameter of nanotube (Fig. 3a) and other distribution concentrated at around 1–3 nm of diameter in a smaller inner diameter of nanotube (Fig. 3b). Similar results have been reported by Kumbhar and coworkers [14], and they thought that the degree of metallic phase was depended on the carbon nanostructure conformation during their work on carbon nanotube-supported ruthenium.

3.3. Hydrogenation of benzene in liquid phase

Hydrogenation of benzene can be represented by the reaction pathway as follows:



In our previous report [15], the Ni-supported carbon nanotubes displayed excellent catalytic performance in the gas phase benzene hydrogenation. In contrast to the reaction in gas phase, the hydrogenation reaction of benzene in liquid phase usually carried out in a continuously operated slurry reactor containing three phases (liquid phase benzene, solid catalyst, and gaseous phase hydrogen). The wetting behaviour of the liquid reactant on solid catalyst will affect immediately the reaction rate. In our experiment, the reactor is too small (only 130 ml) to react completely with hydrogen gas under moderate pressure. We use ethanol as the solvent to increase the ratio of H_2/C_6H_6, therefore the caused solvent effect will decrease the conversion of benzene consumed because of the back-diffusion of the solvent.

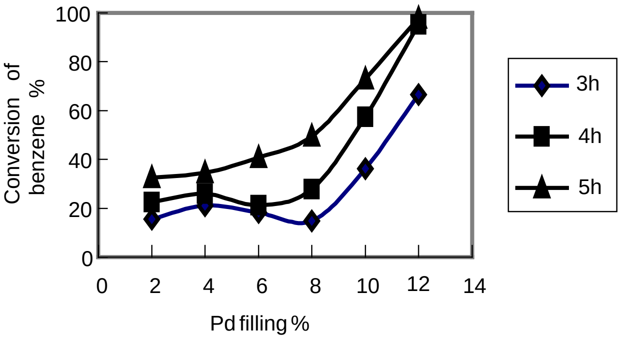


Fig. 4. Conversion of benzene hydrogenation on the different palladium filled in the inner of MWNT at 363 K under moderated pressure.

Fig. 4 shows the conversions of benzene as a function of different Pd filling amount for different reaction time. It can be seen that the conversion of benzene rise rapidly when the amount of palladium salt exceeds 8.0 wt.%, both conversion and selectivity for cyclohexane having achieved up to 100% on the catalyst of 12.0 wt.%.

The turn over of frequency (TOF) values of benzene convert to cyclohexane over different catalysts list in Table 2. It can be seen that all the Pd/CNTs catalysts exhibited higher TOF value than Pd/Y and Pd/AC, and they did not appear obvious fall down tendency within 6 h. Comparing the influence of different palladium amount on the TOF value, the sample with the least amount of nickel has the highest TOF value, it decreases gradually along with increasing the amount of nickel. Due to using the total nickel atoms to calculate the TOF values, it could not show the activity of surface Ni atom. It seems that the nickels exist mainly as active nickels at the lower Ni content, increased nickels are mainly inactive up to the amount of 8.0 wt.%, then increased again active nickels up to 12.0 wt.%. This is considered to be due to that the nickel particles situated at different sites of nanotubes. In our experiment we adopt suitable solvent, make the nickel to firstly enter the inside of nanotubes due

Table 2
TOF[a] value of benzene hydrogenation on different catalysts reaction conditions: 0.1 g catalyst, 12 ml of the ethanol solution containing 5.8 wt.% benzene; $T = 373\,\text{K}$; $p_{H_2} = 1.0\,\text{MPa}$

Catalysts	TOF ($\times 10^{-3}\,s^{-1}$) at different reaction time				
	3 h	4 h	5 h	6 h	Average value
2.0 wt.% Pd/CNT	5.03	5.43	6.29	5.32	5.51
4.0 wt.% Pd/CNT	3.40	3.13	3.34	3.56	3.36
6.0 wt.% Pd/CNT	1.96	1.71	2.62	2.72	2.25
8.0 wt.% Pd/CNT	1.20	1.69	2.39	2.14	1.86
10.0 wt.% Pd/CNT	2.34	2.78	2.87	2.57	2.28
12.0 wt.% Pd/CNT	3.57	3.83	3.15	3.05	3.40
8.0 wt.% Pd/Y	0.65	1.01	0.80	0.65	0.78
8.0 wt.% Pd/AC	0.63	1.02	0.80	0.56	0.75

[a] TOF value means benzene conversion for total nickel in catalyst.

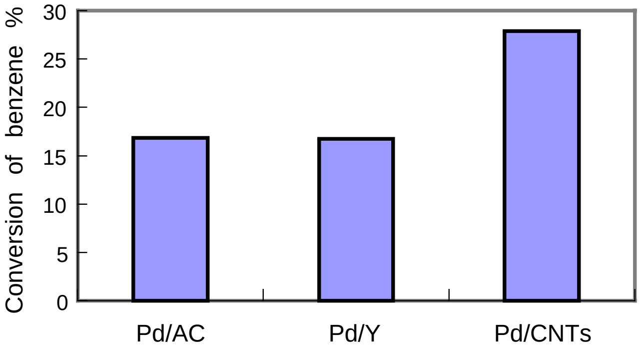


Fig. 5. Conversion of benzene hydrogenation on the metal palladium loaded different supports (activated carbon, Y-type zeolite, and multi-walled carbon nanotubes).

to the strong capillary action of nanotubes, the small clusters form under dilute Pd solution, and the larger particles form under concentrated of Pd solution. When the capillary siphon action achieved equilibrium, the nickels start to deposit on the outer walls of nanotubes under more concentrated solution. Naturally the active nickels initially formed inside of nanotubes exhibit the highest TOF value (2.0 wt.% Pd/CNT). The increased nickels that made the cluster grow up are inactive, and the fresh nickel on the outer of nanotubes are active. The TOF value maintained constant basically during the period also showed that the palladium clusters were steady not to easily aggregate into larger particles, due to the strong interaction between metal clusters and carbon nanotubes possessing a high graphitic content [16]. Furthermore, the metal clusters in the inner of carbon nanotube with one dimension conformation seems that the space effect and the high uptake capacity for hydrogen play also an important role in the hydrogenation reaction.

3.4. Comparison of different supports

For comparison, the catalytic test was also performed on the catalysts of Pd-supported active carbon and Y-type zoelite. The conversion of benzene hydrogenation on different supports was represented in Fig. 5, in which the filling amount is 8.0 wt.% and reaction time is 4 h.

As we can see from Fig. 5 and Table 2, the palladium-filled MWNT catalyst exhibited higher catalytic activity than palladium-supported activated carbon (Pd/AC) and zeolite Y (Pd/Y) under same reaction condition. It depends on the wonderful properties. Firstly the carbon nanotubes have effective specific surface. As shown in Table 1, although the specific surface area (328 m^2/g) of the MWNTs sample, which was pretreated by some processes, is less than that of activated carbon and zeolite Y (900 and 700 m^2/g, respectively), carbon nanotubes possess even pores of several nanometers. Liquid reactants are easy to enter the inner of nanotubes due to capillary siphon action. The specific surface of activated carbon is very large, but the pore distribution is too broad, it is not benefit for high dispersion. Zeolite Y has even micropore and high specific surface, but the wetting ability of liquid benzene on zeolite is less than on carbon materials. Therefore the magnitude of specific surface area is not a main effective factor on the catalytic activity. Secondly, carbon nanotubes have metallic and semi-conductive property, which is favor to the electron transfer and spillover of hydrogen during the process of hydrogenation reaction. Thirdly, the geometric structure of carbon nanotubes also advantages the reaction of benzene hydrogenation and desorption of products. In addition the higher degree of crystallinity of the carbon nanotubes compared to the activated carbon could also explain the high activity obtained on the nanotube-based catalyst [17]. Many researches demonstrated that carbon nanotubes or carbon nanofibers as support of catalyst has exhibited excellent catalytic performance in hydrogenation [18].

It is generally well-known that palladium-based catalysts are efficient for the hydrogenation of the C=C double bond. But due to the high stability of the aromatic rings, many attempts have been made to develop more active catalysts for the benzene hydrogenation. Especially for liquid phase reaction, the lower conversion of benzene relative to gas phase reaction is due to the back-diffusion and solvent effect. Now we developed a novel carrier of catalyst, multi-walled carbon nanotubes with lager inner diameter, active metal may be filled in the inner of them. Different from conventional carriers, it depends on the wonderful properties: (1) effective specific surface areas (over 200 m^2/g); (2) uniform outer diameter about 30–50 nm and lager inner diameter which is big enough to allow any reactants enter and desorption of products; (3) capillary action of particular construction in liquid phase reaction will benefit the wetting and conversion of reactant.

4. Conclusion

In summary, we have proposed a novel liquid benzene hydrogenation catalyst, palladium filled in the inner of multi-walled carbon nanotubes. Palladium clusters were homogenously deposited in the inner surface of MWNT by the wetness impregnation method and displayed spheroidal shape with a mean cluster size centered at 1–8 nm. They exhibited higher activity and higher TOF value than palladium supported on conventional activated carbon and Y-type zeolite. That was mainly attributed to both of wetting action on effective surface and capillary siphon in the nanotubes, and the skeletal structure of carbon nanotubes, owing to having enough space for reaction and desorption of products. According the TOF value and considering the cost, the optimum filling amount is 2.0 wt.%.

Acknowledgements

This work was supported by Korea Foundation of Advanced Study. Authors thank them for their financial support.

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