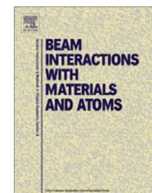
Nuclear Instruments and Methods in Physics Research B 268 (2010) 568–572

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



The effect of ion sputtering of silicon substrates on the catalyst morphology and growth of carbon nanotube arrays

Ruiting Zheng [a,b,*], Yong Zhao [a], Guoan Cheng [a], Kimberlee Collins [b], Matteo Chiesa [b,c]

[a] Key Laboratory of Radiation Beam Technology and Materials Modification of Ministry of Education, College of Nuclear Science and Technology, Beijing Normal University, Beijing 100875, China

[b] Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA

[c] Program of Material Science, Masdar Institute of Science and Technology, Masdar, P.O. Box 54115, Abu Dhabi, United Arab Emirates

ARTICLE INFO

Article history:
Received 5 October 2009
Received in revised form 18 December 2009
Available online 4 January 2010

Keywords:
Carbon nanotubes
Sputter
Catalyst

ABSTRACT

Polished Si substrates are sputtered by He^+ ions, and carbon nanotube arrays are prepared on the Fe-coated substrates by heat chemical vapor deposition from acetylene. Scanning electron microscopy and atomic force microscopy are employed to examine the morphologies of sputtered substrates, catalyst and carbon nanotube arrays. It is found that ion sputtering is effective in increasing the roughness of Si substrates, and helpful in obtaining higher density Fe catalyst particles and better-aligned carbon nanotube arrays.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Since Ijima published the landmark paper of carbon nanotubes (CNTs) [1], CNTs have attracted attention in the scientific community because of their unique structural, electrical, mechanical, physical and chemical properties. Numerous papers have reported [2,3] that CNT arrays are an excellent field emitter with low threshold voltage and high emission current, and for this reason they can be employed as cold-cathode flat panel displays and vacuum microelectronic devices. Furthermore, the synthesis of CNT arrays on Si substrates is entirely compatible with existing semiconductor process, which opens opportunities for integrating CNTs with semiconductor devices.

Ajayan et al. [4] obtained quasi-aligned CNTs by cutting CNT composites. Subsequently, much progresses has been made in synthesizing CNT arrays. De Heer et al. [5] aligned CNTs by drawing tube suspensions in ethanol through a 0.2 μm pore ceramic filter. Li et al. [6] grew vertically aligned CNT arrays using chemical vapor deposition (CVD) methods on a mesoporous substrate. At present, CVD methods are frequently employed in synthesizing vertically aligned CNT arrays. In these methods, a transition metal film is deposited on a porous or plane substrate as a catalyst, and then CNT arrays are grown in a CVD system. Porous substrates include porous Si [7], zeolite [8] and porous Al_2O_3 [9]. Mesopores define the size of the catalyst particles and the precipitation direction of carbon atoms. The presence of mesopores results in the growth of well-aligned CNT arrays, but at the same time, adds cost and difficulty to the CNT manufacturing process.

It is convenient to synthesize aligned CNTs on Si wafers using a CVD system. This method has the potential for large-scale synthesis. But low adhesion between CNTs and substrates makes it easy to tear CNTs off from the substrates, and results in device failures [10]. Recent work [11] found that low density and poor morphology of CNTs in direct contact with the substrate, are among the major reasons for failures.

To solve this problem, deposition of low work-function materials at the tips of the CNTs to terminate the growth of CNT arrays is employed together with other post-growth processing methods [11–13]. Here we show that higher density and well-aligned CNT arrays can be simply achieved by pre-treating the substrates [14] before the CNT growth. We employ He^+ ion sputtering of the Si substrates, followed by a thin Fe film deposition before CNT arrays are grown on the substrates. The influence of ion sputtering on the growth of CNT arrays is investigated by comparing the results from experiments carried out simultaneously on pre-treated and untreated Si substrates.

2. Experimental

Two p-type Si(1 0 0) polished wafers with a resistivity of 15 Ω cm were used as substrates in this study. One wafer was

* Corresponding author. Address: Key Laboratory of Radiation Beam Technology and Materials Modification of Ministry of Education, College of Nuclear Science and Technology, Beijing Normal University, Beijing 100875, China. Tel./fax: +86 10 62205403.
E-mail address: rtzheng@bnu.edu.cn (R. Zheng).

0168-583X/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2009.12.015

pre-treated in a Matrix® reactive ion etching system (commercial RIE reactor) and exposed to He^+ plasma with the following conditions: a substrate temperature of 473 K, a pressure of 10 Pa, rf power of 150 W, an exposure time of 20 min. Then, the pre-treated wafer and the untreated wafer were divided into $10 \times 10\,mm^2$ pieces for further investigation.

Thin Fe films (5–10 nm) were deposited on the pre-treated and untreated substrates at the same time by a metal vapor vacuum arc ion deposition system. Before deposition, substrates were bombarded by Fe ions to get clean surfaces. The synthesis of CNT arrays was carried out in a horizontal CVD system. Pre-treated and untreated Si substrates were placed in a quartz boat simultaneously, and transferred into the middle of the reaction chamber. The reaction zone was heated to 750 °C in a N_2 gas environment. Then, H_2 gas was introduced to deoxidize the Fe catalyst for 30 min. Mixtures of C_2H_2 and H_2 gas in 75/400 ratios were then introduced into the reaction chamber for 40 min. After conducting experiments, the samples were cooled slowly in the furnace in a H_2 gas environment. The purities of the gases employed in the experiment are all higher than 99.5%.

The surface roughness of the substrates was examined by a Nanoscope IIIa atomic force microscope (AFM). The morphologies of catalyst films were observed by a XL30S-FEG field emission scanning electron microscope (FESEM). The morphologies of CNT arrays were observed using a S-3500 N scanning electron microscope (SEM). The substrate surface roughness, catalyst particle diameter, the length and diameter of CNTs presented in paper are statistically calculate from 6 images which were taken from different locations and different samples.

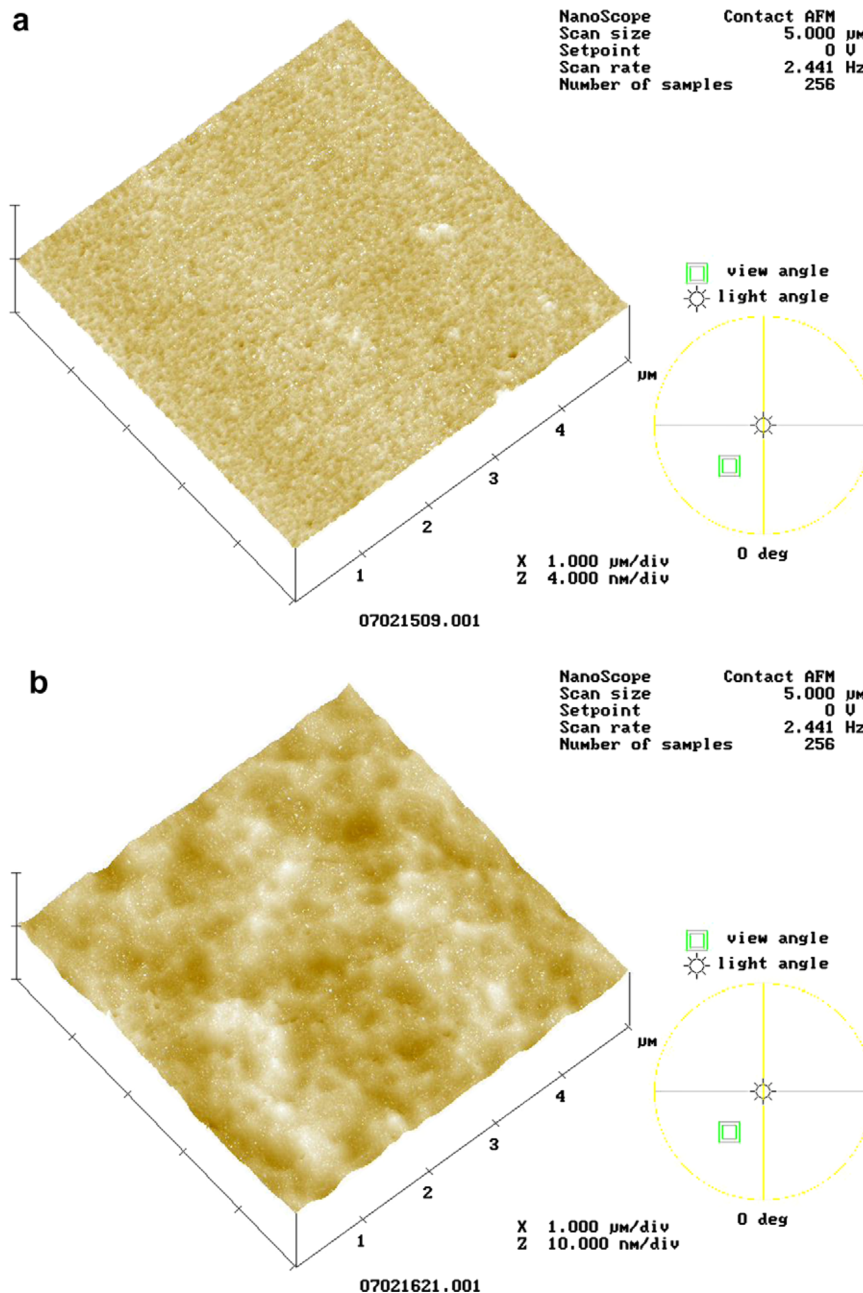


Fig. 1. AFM images of the untreated and pre-treated Si wafers. (a) AFM image of the untreated Si wafer, whose mean roughness is about 0.06 nm, and (b) AFM image of the pre-treated Si wafer, whose mean roughness is about 0.43 nm.

3. Results and discussion

3.1. Influence of ion sputtering on catalyst morphology

He^+ ions accelerated by an applied electric field bombard the Si wafer surfaces, and Si surface atoms were sputtered by the corresponding energy transfer. Fig. 1 shows the AFM images of the untreated and pre-treated Si wafers. By the comparison of Fig. 1a and b, one can observe that the surfaces of the Si wafers became rough after He^+ ion sputtering. Mean roughness increases from the original roughness of 0.06 to 0.43 nm.

The surface roughness of the substrates will noticeably affect the morphology of Fe films in further heat treatments. Fig. 2 shows the FESEM images of 5 and 10 nm Fe films deposited on the different Si substrates after 30 min of annealing at 750 °C. It can be observed that the Fe films break into particle films as a consequence of the annealing treatment, and the size and density of Fe particles on different substrates are different. Fig. 2a shows the morphology of 5 nm Fe film on an untreated Si wafer substrate. Fe particle size is inhomogeneous in this picture. The bigger particles reach 300 nm in diameter, but the smaller particles are only about 50 nm, and the average Fe particle size is about 138 nm. Fig. 2b shows the morphology of the Fe film deposited on a pre-treated Si substrate. The size distribution of Fe particles on the pre-treated substrate is much narrower than on the untreated Si substrate. Only a few bigger particles can be found on the substrate, and the average size of Fe particles is about 72 nm. In addition to having different particle sizes, the average density of the catalyst in Fig. 2b is about 87.65 particles/μm^2, which is much higher than the average density of 19.91 particles/μm^2 found in Fig. 2a. Fig. 2c and d shows the morphology of 10 nm Fe films on untreated and pre-treated Si wafer substrates, respectively. The average particle size in Fig. 2c is about 98 nm, and the average density is about 38.08 particles/μm^2. In Fig. 2d, the average particle size is about 89 nm, and the average density is about 41.67 particles/μm^2. The morphologies of 10 nm Fe films on untreated and pre-treated Si wafer substrates look comparable, with the exception that more big particles exist in Fig. 2c, and the average particle density in Fig. 2d is little higher than that in Fig. 2c.

Films have the tendency to reduce their surface energy by agglomerating. During annealing at 750 °C, the Fe films tend to break, shrink, and form particles. An untreated, polished Si surface has a low threshold for the movement of Fe atoms, and allows Fe films easy to diffuse, agglomerate and transform into large particle films during annealing. Ion sputtering increases the surface roughness of the Si substrate, and enhances the potential barrier for the movement of Fe atoms. Ion sputtering hinders the atoms' diffusion, allowing for further growth of Fe particles, and helps the formation of Fe particle films with fine dimensions and uniform distributions. When the initial Fe film thickness is about 10 nm, the influence of the substrates' roughness on CNT arrays is less obvious. We believe that the surface potential barrier induced by ion sputtering was not sufficient to hinder the agglomeration of Fe particles in the annealing of 10 nm Fe films.

3.2. Influence of ion sputtering on the growth of CNT arrays

In order to determine the effect of ion sputtering on the growth of CNT arrays, CNTs were synthesized on untreated and pre-treated substrates under the same conditions. Two thicknesses of Fe films (5 and 10 nm) were deposited on different Si substrates. The growth temperature was set to 750 °C in a C_2H_2/H_2 environment. The C_2H_2/H_2 ratio was controlled at 75/400 ml/min, and the growth time was 40 min. Fig. 3 shows SEM images of the sample sections.

Fig. 3a shows an SEM image of CNTs grown on a polished substrate coated with a 5 nm Fe film. It can be seen that the tubes are about 6 μm long and curved. The average diameter of these tubes is about 60 nm. Long and well-aligned tubes are obtained on the pre-treated Si substrate, as shown in Fig. 3b. The average length of CNTs in Fig. 3b reaches 80 μm and the average diameter is about 65 nm. For a 10 nm catalyst film, however, the influence of the sub-

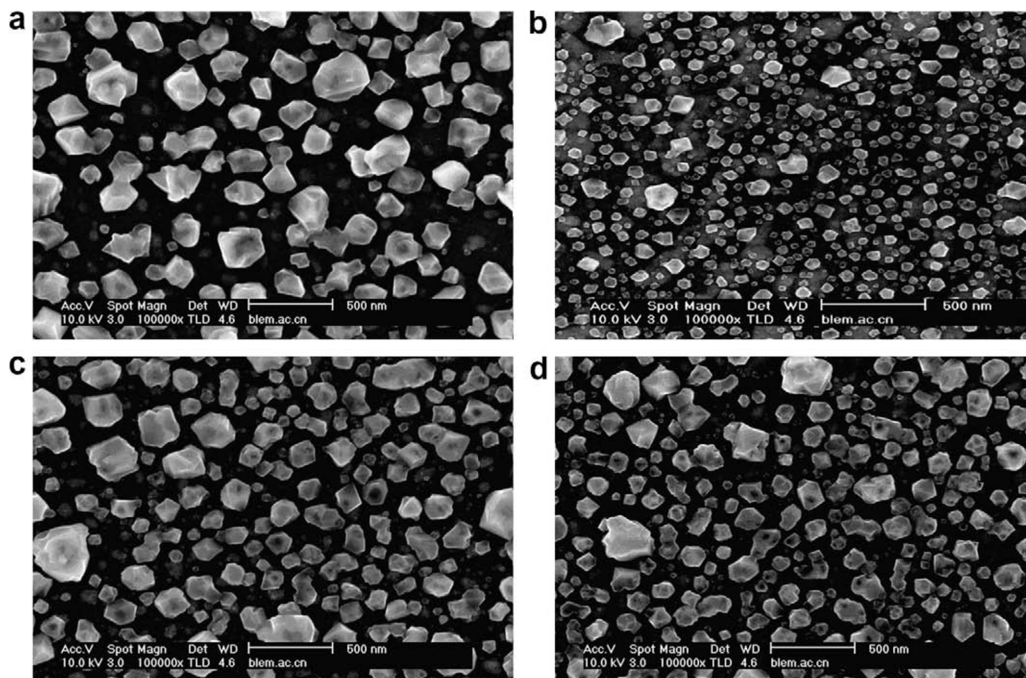


Fig. 2. FESEM images of 5 and 10 nm Fe films deposited on different Si substrates after 30 min of annealing at 750 °C. (a) 5 nm Fe film deposited on an untreated Si substrate, (b) 5 nm Fe film deposited on a pre-treated Si substrate, (c) 10 nm Fe film deposited on an untreated Si substrate, and (d) 10 nm Fe film deposited on a pre-treated Si substrate.

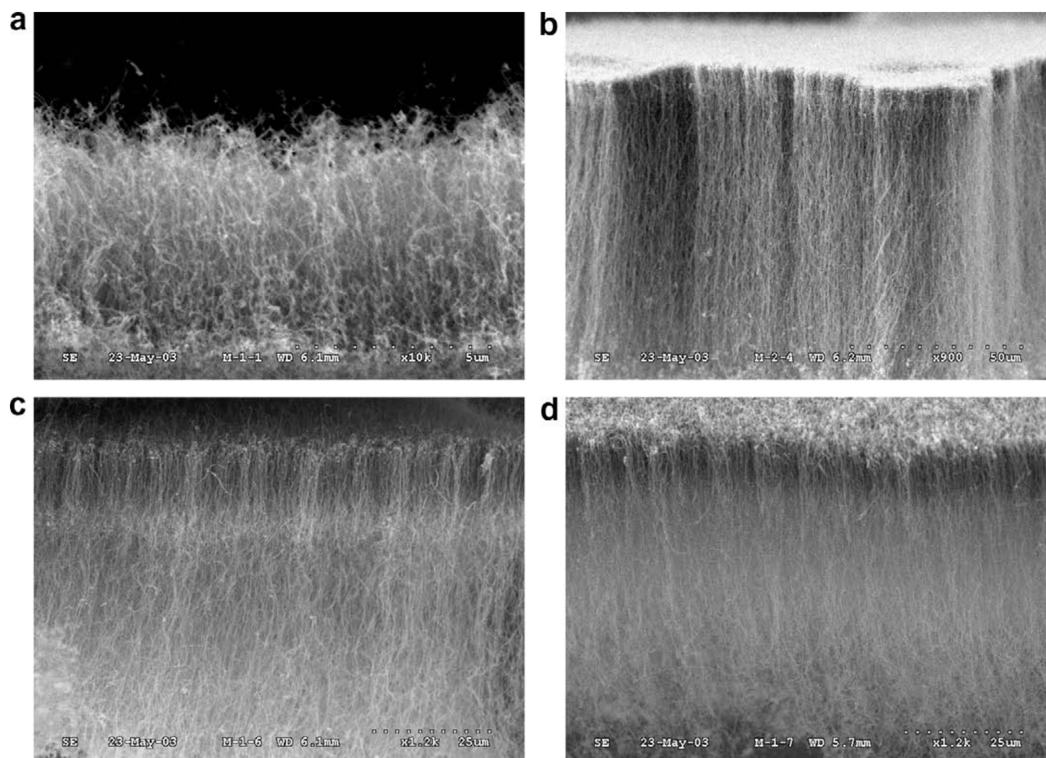


Fig. 3. SEM photographs of CNTs grown on various substrates. (a) CNTs grown on an untreated Si substrate coated in a 5 nm Fe film, (b) CNTs grown on a pre-treated Si substrate coated in a 5 nm Fe film, (c) CNTs grown on an untreated Si substrate coated in a 10 nm Fe film, and (d) CNTs grown on a pre-treated Si substrate coated in a 10 nm Fe film.

strate is less evident. Fig. 3c and d shows SEM images of CNT arrays grown on polished and sputtered substrates coated with 10 nm Fe films, respectively. Dimensions of CNTs are comparable on both substrates. The CNTs are about 70 μm long and 80 nm in diameter. The arrays in Fig. 3c and d are not as well-aligned as those shown in Fig. 3b. One can observe that the particles are bigger than the diameter of the CNTs. The diameter of the CNTs is determined by the Fe particle size after 30 min of reduction. After this time, the furnace needs six extra hours to cool down from 750 °C to room temperature. The diffusion rate of iron atoms is higher at higher temperature. If the Fe particles are furnace cooled from 750 °C, they will grow further. Nevertheless the influence of the substrate roughness on the particle size has the same characteristics.

From the above results, it can be seen that the rough surface induced by sputtering helps the formation of fine and high density catalyst particles for a 5 nm initial Fe film, and further helps the growth of denser, longer and better-aligned CNT arrays. According to our previous investigation [15,16], the density of CNTs is proportional to the density of the Fe particles. Higher density catalyst particles provide more opportunity for CNT growth. Higher CNT density leads to better alignment and longer CNTs, because Van der Waals interaction between CNTs provide the overall driving force for oriented growth of CNTs.

The particle density of 10 nm annealed Fe film is higher than the density of 5 nm annealed Fe film on untreated Si substrates, but less than the density of 5 nm annealed Fe film on ion sputtered Si substrates. A difference of catalyst particle densities makes the CNT arrays in Fig. 3c and d more densely packed compared to that in Fig. 3a, but less densely packed than that in Fig. 3b. In order to obtain more dense and well-aligned CNT arrays on a 10 nm Fe film coated pre-treated Si substrate, higher power and a longer period of sputtering are needed to make a rougher substrate surface.

Finally, we would like to point out that the approach demonstrated here is not specific to CNTs. In the case of the growth of nanowires (NWs), which involves a vapor–liquid–solid (VLS) mechanism, it is difficult to control the catalyst size and density on polished Si wafers at the same time. For thin catalyst films, smaller average catalyst size can be obtained after annealing treatment, but low catalyst density makes NW arrays short and curved. The process employed in this paper provides a method to control the catalyst size and density simultaneously by controlling the initial catalyst film thickness and substrate roughness. The method demonstrated here can be easily applied to a variety of 1D NW arrays.

4. Conclusions

He^+ ion sputtering is employed to pre-treat Si substrates. CNT arrays were then prepared on both pre-treated and untreated Si substrates. Based on the investigations of the substrates, catalysts and CNT arrays, it is found that ion sputtering is useful in increasing the roughness of Si substrates, allowing us to obtain fine and uniform catalyst particles, and finally produce well-aligned CNT arrays. The method demonstrated here can be easily applied to a variety of 1D nanowire arrays.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 10575011, 10576003), China scholarship fund and Beijing Nova project of Science and Technology.

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] P.G. Collins, A. Zettl, Appl. Phys. Lett. 69 (1996) 1969.
[3] Q.H. Wang, T.D. Corrigan, J.Y. Dai, R.P.H. Chang, Appl. Phys. Lett. 70 (1997) 3308.
[4] P.M. Ajayan, O. Stephan, C. Colliex, D. Trauth, Science 265 (1994) 1212.

[5] W.A. de Heer, W.S. Bacsa, A. Chatelain, T. Gerfin, R. Humphrey-Baker, L. Forro, D. Ugarte, Science 268 (1995) 845.
[6] W.Z. Li, S.S. Xie, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Science 274 (1996) 1701.
[7] S.S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, H. Dai, Science 283 (1999) 512.
[8] K. Mukhopadhyay, A. Koshio, T. Sugai, N. Tanaka, H. Shinohara, Z. Konya, J.B. Nagy, Chem. Phys. Lett. 303 (1999) 117.
[9] C. Wang, M. Li, S. Pan, H. Li, Chin. Sci. Bull. 45 (2000) 493.
[10] W. Wei, K.L. Jiang, Y. Wei, M. Liu, H.T. Yang, L.N. Zhang, Q.Q. Li, L. Liu, S.S. Fan, Nanotechnology 17 (2006) (1994).
[11] K. Liu, K. Jiang, Y. Wei, S. Ge, P. Liu, S. Fan, Adv. Mater. 19 (2007) 975.
[12] Y.M. Liu, S.S. Fan, Nanotechnology 15 (2004) 1033.
[13] E. Minoux, O. Groening, K.B.K. Teo, S.H. Dalal, L. Gangloff, J.-P. Schnell, L. Hudanski, I.Y.Y. Bu, P. Vincent, P. Legagneux, G.A.J. Amaratunga, W.I. Milne, Nano Lett. 5 (2005) 2135.
[14] F. Granone, V. Mussi, A. Toma, S. Orlanducci, M.L. Terranova, C. Boragno, U. Buatier de Mongeot, C. Valbusa, Nucl. Instr. Meth. B 230 (2005) 545.
[15] R.T. Zheng, G.A. Cheng, Y.B. Peng, Y. Zhao, H.P. Liu, C.L. Liang, Sci. Chin. E 47 (2004) 616.
[16] H.P. Liu, G.A. Cheng, R.T. Zheng, Y. Zhao, J. Mol. Catal. A 247 (2006) 52.