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Kinetics of Photocatalytic Degradation of *p*-Toluene Sulfonic Acid on TiO_2 Surface

HONGXIA CAO* and QINGZHEN FENG

College of Chemistry and Chemical Engineering, Kaifeng University, Kaifeng 475004, Henan Province, P.R. China

*Corresponding author: Fax: +86 378 3655896; Tel: +86 378 3810041; E-mail: chx@kfu.edu.cn

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In present work, the photocatalytic degradation of *p*-toluene sulfonic acid was investigated in aqueous solutions containing TiO_2 suspension as photocatalyst, especially the kinetics was discussed. The effects of the various operating parameters including initial concentration of *p*-toluene sulfonic acid, pH value, TiO_2 concentration and irradiation intensity *etc.*, were studied. Results showed that the kinetics of photocatalytic degradation of *p*-toluene sulfonic acid in the presence of TiO_2 was in accord with first-order Langmuir-Hinshelwood model when the initial concentration of *p*-toluene sulfonic acid was lower than 100 mg/L. The apparent degradation rate constants decreased with increase of the initial concentration of *p*-toluene sulfonic acid and displayed with one-peak pattern with the increases of TiO_2 concentration and aqueous pH value. As the increasing concentration of *p*-toluene sulfonic acid, a trend that the degradation reaction transferred from first-order to zeroth-order reaction model was observed. The optimal operating parameters were consisted of pH at 3 and TiO_2 of 100 mg/L. It was also observed that the presence of air could accelerate the degradation rate dramatically.

Key Words: TiO_2, *p*-Toluene sulfonic acid, Photocatalysis, Kinetics.

INTRODUCTION

As an important chemical raw material and intermediate, *p*-toluene sulfonic acid (*p*-TSA) has been widely used in the fields of pesticides, pharmaceuticals, dyes, catalyst, plastic, resin *etc*. Industries, which produced *p*-toluene sulfonic acid or use *p*-toluene sulfonic acid as raw or intermediate, always discharged large amounts of wastewater including *p*-toluene sulfonic acid[1,2]. However, *p*-toluene sulfonic acid had moderate toxicity, resulting in irritation to human skin, eyes and mucosa. Therefore *p*-toluene sulfonic acid is hazardous material and its discharge should be strictly controlled as possible. *p*-Toluene sulfonic acid is a typical biorefractory toxicoid[3], with strong polarity and high water solubility, so it is difficult to be eliminated by conventional methods such as flocculation, extraction and adsorption. At present, the treatment of such industrial wastewaters is still challenged.

As a green and environment-friendly technique, photocatalysis has received enormous attention in water and wastewater treatment for several decades[4-6]. TiO_2 was also proved to be the most promising photocatalyst because of its high efficiency on removal of organic pollutants. Particularly, TiO_2 is low cost, stable and harmless and the operating condition is moderate.

There are few reports on the degradation of *p*-toluene sulfonic acid. Son *et al.*[7] investigated the oxidation degradation of *p*-toluene sulfonic acid using thermally activated hydrogen peroxide and proposed a detailed degradation reaction mechanism. Brezová *et al.*[2] and Kais *et al.*[8] studied the photocatalytic decomposition of *p*-toluene sulfonic acid in aqueous titanium dioxide suspensions and in systems containing immobilized TiO_2 particles. Kamble *et al.*[9] also conducted the photocatalytic degradation of *p*-toluene sulfonic acid using concentrated solar radiation in slurry photoreactor. Though these works have been done, the in-depth kinetics of the degradation of *p*-toluene sulfonic acid on TiO_2 has been rarely reported. So in the present work, the degradation behaviour of *p*-toluene sulfonic acid using TiO_2 as photocatalyst under UV irradiation was investigated, with the initial concentration of *p*-toluene sulfonic acid, pH, TiO_2 concentration as variables. The kinetics parameters of degradation were calculated by fitting the experimental data to adapt to Langmuir-Hinshelwood (L-H) model.

EXPERIMENTAL

p-Toluene sulfonic acid (*p*-TSA), analytical grade, was obtained from Shanghai Sanpu Chemical Industry Co., Ltd. TiO_2, anatase > 99 %, with 5-10 nm of particle size and 210 ± 10 m^2/g of specific surface area, was from Zhejiang Hongsheng Material Technology Co., Ltd.

All the other reagents were used without further treatment and high purity water was used throughout.

Methods: The experiments were carried out on a SGY-I multifunctional photochemical reaction (Nanjing Sidongke

Electrical Equipment Co., Ltd.; high-pressure mercury lamp, 300 W, main wavelength 254 nm). A solution containing known concentration of *p*-toluene sulfonic acid and TiO_2 was prepared and it was allowed to equilibrate for 0.5 h, then 50 mL of the prepared suspension was transferred to the reactor. The variables were involved with initial concentration of *p*-toluene sulfonic acid, TiO_2 concentration and pH. pH of the suspension (measured with a HI 98128 pH meter, HANNA, Italy) was adjusted by adding a little H_2SO_4 or NaOH solution. At certain reaction intervals, 5 mL of sample was withdrawn and centrifuged at 8000 rpm for 10 min. The residual *p*-toluene sulfonic acid concentration was analyzed on an UV-2000 spectrometer (Lab Tech, Beijing, China)[10]. All the experiments were performed with bubbling air under 0.5 MPa of air partial pressure using an Air compressor (Shanghai Aotusi Industry and Trade Co., Ltd.).

RESULTS AND DISCUSSION

Effect of Initial Concentration of *p*-toluene sulfonic acid. Generally, the photocatalytic kinetics of the process that used TiO_2 as catalyst was described by Langmuir-Hinshelwood (L-H) equation[11-13], which was given as,

$$r = \frac{-dc}{dt} = \frac{kKc}{(1+Kc)} \quad (1)$$

where r is the reaction rate, c is the concentration of reactant at time t, k is the reaction rate constant and K is the adsorption constant.

According to the level of the concentration of the reactant, the kinetics always was shown with two forms, namely, zeroth-order and first-order forms. At high level of concentration of the reactant, Kc >> 1, it shows as zeroth-order form as follow,

$$r = \frac{-dc}{dt} = k \quad (2)$$

and on the contrary, Kc << 1, it shows as first-order form as follow,

$$r = -\frac{dc}{dt} = kKc \quad (3)$$

After definite integration by applying the initial conditions, eqns. 2 and 3 can be writen as,

$$c = c_0 - kt + a \quad (4)$$

$$\ln\frac{c_0}{c} = kKt + b = K_{ap}t + b \quad (5)$$

where K_{ap} represents the apparent reaction rate constants, c_0 represents the initial concentration of *p*-toluene sulfonic acid and a and b are constants of integration.

Fig. 1 shows that plots of normalized concentration of *p*-toluene sulfonic acid (c/c_0) with reaction time (t). It was observed that the plots of c/c_0 *vs.* t yielded a straight line when initial *p*-toluene sulfonic acid concentrations were higher than 130 mg/L, suggested the kinetics under these conditions could be well expressed by zeroth-order L-H equation. However, the plots of c/c_0 *vs.* t were observed to be close to logarithmic relationship when initial *p*-toluene sulfonic acid concentrations were lower than 100 mg/L, namely, the kinetics might confirm to first-order L-H equation. Table-1 listed the kinetics parameters that fitted by zeroth-order and first-order L-H equations.

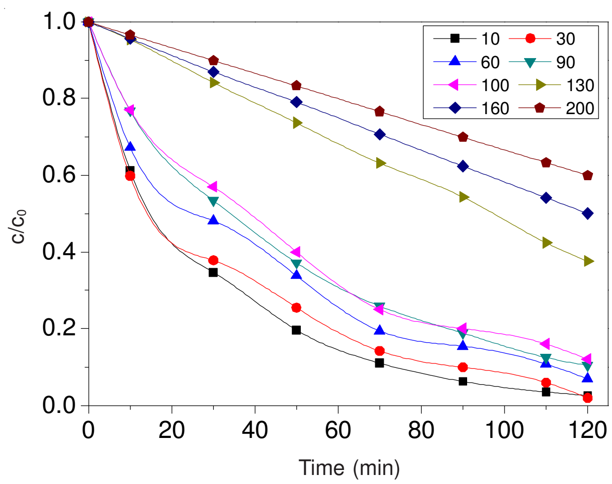

Fig. 1. Effects of initial concentration of *p*-toluene sulfonic acid (mg L^{-1}). TiO_2 concentration, 100 mg L^{-1}; pH, 7.0

As illustrated in Table-1, it is obvious that the experimental data are well fitted by zeroth-order L-H equation at high initial *p*-toluene sulfonic acid concentration (130-200 mg/L) and by first-order L-H equation at low initial *p*-toluene sulfonic acid concentration (10-100 mg/L), with the linear correlation coefficient (R) > 0.99. It can also be seen that k for zeroth-order L-H model and K_{ap} for first-order L-H model decrease with the increasing initial concentration of *p*-toluene sulfonic acid. This might be attributed to the adsorption of *p*-toluene sulfonic acid on TiO_2 surface has been equilibrated to saturation when the initial concentration of *p*-toluene sulfonic acid amount to 10 mg/L. Though the increasing concentration of *p*-toluene sulfonic acid promoted the transfer of *p*-toluene sulfonic acid from aqueous to catalyst's surface, but much more intermediates were formed. These intermediates adsorbed on the surface of

TABLE-1
KINETIC EQUATIONS WITH VARIOUS INITIAL OF *p*-TOLUENE SULFONIC ACID

c_0 (mg L^{-1})	Zeroth-order L-H equation			First-order L-H equation		
	Kinetic equation	k (mg L^{-1} min^{-1})	R	Kinetic equation	K_{ap} (min^{-1})	R
10	c = 7.076 – 0.0681t	0.0681	0.8863	ln c_0/c = 0.0285t + 0.2034	0.0285	0.9988
30	c = 21.65 – 0.201t	0.201	0.9016	ln c_0/c = 0.0244t + 0.1636	0.0244	0.9945
60	c = 46.81 – 0.403t	0.403	0.9312	ln c_0/c = 0.0198t + 0.1186	0.0198	0.9943
90	c = 74.75 – 0.617t	0.617	0.9507	ln c_0/c = 0.0181t + 0.08217	0.0181	0.9959
100	c = 83.90 – 0.675t	0.675	0.9516	ln c_0/c = 0.0170t + 0.06395	0.0170	0.9960
130	c = 130.1 – 0.676t	0.676	0.9981	ln c_0/c = 0.00802t – 0.05237	0.00802	0.9893
160	c = 159.6 – 0.663t	0.663	0.9992	ln c_0/c = 0.00570t – 0.02448	0.00570	0.9953
200	c = 198.9 – 0.666t	0.666	0.9997	ln c_0/c = 0.00423t – 0.01447	0.00423	0.9973

catalyst and competed with the parent *p*-toluene sulfonic acid. However, for constant light intensity, a high concentration of reactant could also enhance the photon be adsorbed by the solution, resulting in the utilization of photon became weak. Each of these factors could decrease the reaction rate. The reaction rates are fast at low initial concentration of *p*-toluene sulfonic acid, but the degradation amount of *p*-toluene sulfonic acid is relatively fewer. So the concentration of *p*-toluene sulfonic acid should be taken into account in practical application.

Effect of TiO_2 concentration. The effect of TiO_2 concentration on the photocatalytical degradation of *p*-toluene sulfonic acid was studied using 40, 60, 80, 100, 160 and 200 mg/L concentrations of TiO_2 and 100 mg/L initial concentration of *p*-toluene sulfonic acid. Fig. 2 shows the plots of c/c_0 *vs.* t. Fig. 2 showed the degradation ratio increased with increasing TiO_2 concentration from 40 to 100 mg/L, while decreased sharply from 100 to 200 mg/L. When the experimental data were adapted to first-order L-H equation, the K_{ap} was calculated (Table-2). In all cases, R values are higher than 0.99, which confirmed the first-order L-H kinetics model for photocatalytic degradation of *p*-toluene sulfonic acid in the presence of TiO_2.

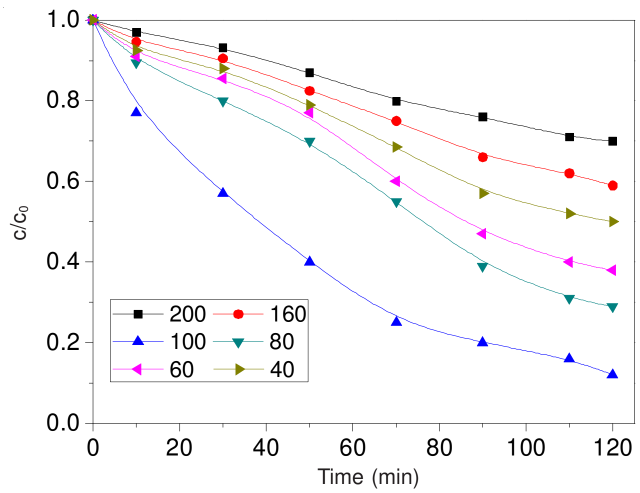

Fig. 2. Effect of TiO_2 concentration (mg L^{-1}). pH, 7; initial concentration of *p*-toluene sulfonic acid, 100 mg L^{-1}

TABLE-2
KINETIC EQUATIONS WITH VARIOUS TiO_2 CONCENTRATION

TiO_2 (mg L^{-1})	Kinetic equation	K_{ap} (min^{-1})	R
40	$\ln c_0/c = 0.00596t - 0.01967$	0.00596	0.9946
60	$\ln c_0/c = 0.00844t - 0.04261$	0.00844	0.9942
80	$\ln c_0/c = 0.0107t - 0.06838$	0.01071	0.9903
100	$\ln c_0/c = 0.0170t + 0.06395$	0.01703	0.996
160	$\ln c_0/c = 0.00445t - 0.01124$	0.00361	0.9945
200	$\ln c_0/c = 0.00306t - 0.00613$	0.00306	0.9963

As seen from Table-2, k increased gradually with increasing dosage of TiO_2 from 40 to 100 mg/L and then decreased when the dosage of TiO_2 was more than 100 mg/L. The reason of this observation is thought to be that at the concentration range from 40 to 100 mg/L the enhancement in K_{ap} is probably due to an increased number of available photogenerated electrons and holes and a further increase of catalyst loading may cause opacity and light reflecting and scattering, thus decrease in the passage of irradiation through the solution. San *et al.* reported the excessive TiO_2 might also cause the aggregation TiO_2 particles[14], thus decrease the reaction sites. In the present work, TiO_2 concentration was selected at 100 mg/L.

Effect of pH: The pH value is an important influencing factor in the degradation process of *p*-toluene sulfonic acid, because it determines not only the existing forms of *p*-toluene sulfonic acid in aqueous solution but also the surface charge state of TiO_2. The experiments were carried out using initial *p*-toluene sulfonic acid concentration of 100 mg/L and TiO_2 concentration of 100 mg/L. pH was varied at 1, 3, 5 7, 9 and 11. Fig. 3 shows the plots of c/c_0 *vs.* t at different pH. As seen from Fig. 3, the degradation ratio was found to be the highest when the pH was at 3. Table-3 lists the first-order L-H kinetic parameters as function of aqueous pH.

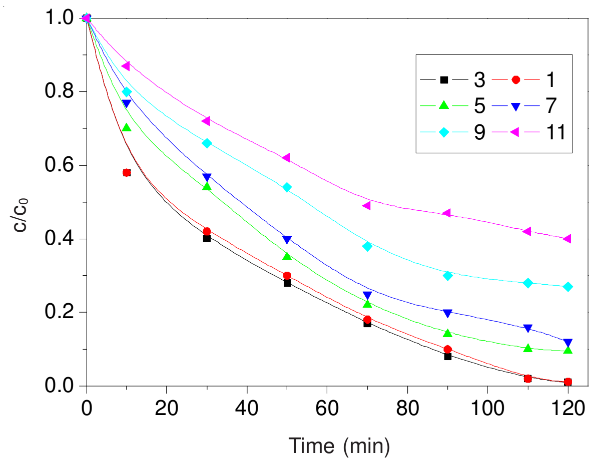

Fig. 3. Effect of pH. Initial concentration of *p*-toluene sulfonic acid, 100 mg L^{-1}; TiO_2 concentration, 100 mg L^{-1}

TABLE-3
KINETIC EQUATIONS WITH VARIOUS INITIAL AQUEOUS pH

pH	Kinetic equation	K_{ap} (min^{-1})	R
1.0	$\ln c_0/c = 0.03179t + 0.05267$	0.03198	0.9923
3.0	$\ln c_0/c = 0.03339t + 0.1214$	0.03339	0.9910
5.0	$\ln c_0/c = 0.01998t + 0.07132$	0.01998	0.9964
7.0	$\ln c_0/c = 0.01703t + 0.06395$	0.01703	0.9960
9.0	$\ln c_0/c = 0.01101t + 0.07934$	0.01101	0.9916
11	$\ln c_0/c = 0.00746t + 0.06962$	0.00746	0.9911

It shows that the K_{ap} increases with pH increases from 1-3, which as further pH increases from 3-11, K_{ap} decreases. The adsorption of *p*-toluene sulfonic acid on the surface of TiO_2 is mainly through the functional group like the SO_3H. The pKa of *p*-toluene sulfonic acid is 3.09. When the pH is around pKa, neutral *p*-toluene sulfonic acid dominates so as to favour for the adsorption process. On the other hand, a suitable acidic pH is advantageous to form $TiOH_2^+$ groups on surface of TiO_2[15], which is favourable for generating ·OH. However, the much stronger acidity might lead to high-density of $TiOH_2^+$ groups, which would adsorb the intermediates to hinder the degradation of parent compound.

Effect of irradiation intensity: As seen from Fig. 4, the irradiation intensity is of great advantages to degradation ratios, which increases with the increase of irradiation intensity. At the first 90 min, degradation ratios of 30, 300 and 500 W irradiation are amount to 20.2, 90.0 and 99.8 %, respectively. This is owing to that as the irradiation intensity increase, the photons reaching to TiO_2 surface increase and more electron-

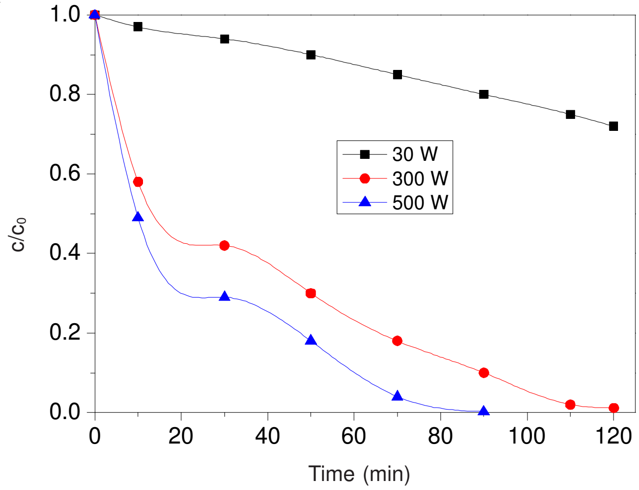

Fig. 4. Effect of irradiation intensity. Initial concentration of *p*-toluene sulfonic acid, 100 mg L^{-1}; TiO_2 concentration, 100 mg L^{-1}; pH, 3

hole pair form. So under the same condition, the stronger the irradiation intensity is, the higher the degradation ratio is.

Effect of aeration: Under the optional conditions, air, oxygen or none were bubbled into degradation systems to in-vestigate the influence of aeration. Results are shown in Fig. 5, the degradation ratios are in the order of oxygen ≥ air > none. The aeration could make the suspension systems more uniform, which are beneficial to photons reaching to TiO_2 surface and accelerate the adsorption and desorption of reactants and products, thus enhance the degradation ratios. On the other hand, oxygen, as an electron trapping agent, O_2 could trap the photogenerated electrons and hinder the combination of electrons and holes, which will increase the chance of the formation of ·OH[16]. Instead of air with oxygen, the degradation ratio of *p*-toluene sulfonic acid at each interval has no significant increase, so, bubbling air is more suitable, when TiO_2 was selected to photocatalytic treatment wastewater including *p*-toluene sulfonic acid.

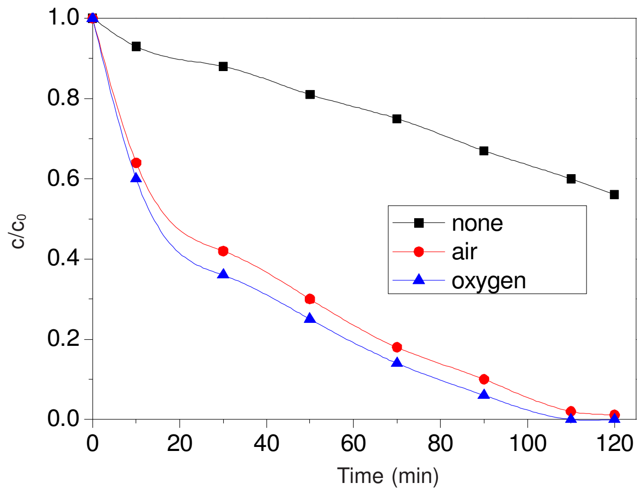

Fig. 5. Effect of aeration. Initial concentrations of *p*-toluene sulfonic acid, 100 mg L^{-1}; TiO_2 concentration, 100 mg L^{-1}; pH, 3

Conclusion

The photocatalytic degradation of *p*-toluene sulfonic acid was investigated in aqueous solutions containing TiO_2 suspension as photocatalyst. It was found that the initial concentration of *p*-toluene sulfonic acid, pH, TiO_2 concentration and irradiation intensity were important influence factors that affected degradation rates. The kinetics of photocatalytic degradation of *p*-toluene sulfonic acid in the presence of TiO_2 was found to be in good agreement with Langmuir-Hinshelwood model. The *p*-toluene sulfonic acid could be best degraded included the conditions of pH around 3, which is very close to the pK_a of *p*-toluene sulfonic acid and TiO_2 concentration of 100 mg/L. The apparent degradation rate constants decreased with increase of the initial concentration of *p*-toluene sulfonic acid and displayed with one-peak pattern with the increases of TiO_2 concentration and aqueous pH value. The results obtained in this work were expected to supply technical supports for the advanced treatment of *p*-toluene sulfonic acid wastewater.

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REFERENCES

1. I. Bouzaida, C. Ferronato, J.M. Chovelon, M.E.Rammah and J.M. Herrmann, *J. Photochem. Photobiol. A: Chem.*, **168**, 23 (2004).
2. V. Brezova, M. Jankovicova, M. Soldan, A. Blazkova, M. Rehakova, I. Surina, M. Ceppan and B. Havlinova, *J. Photochem. Photobiol. A: Chem.*, **83**, 69 (1994).
3. S. Chang, S. Chen and Y. Huang, *Phys. Chem. C,* **115**, 1600 (2011).
4. Q. Chen, F. Wang, J.M. Song and J.Y. Yuan, *Acta Sci. Circumstant.,* **29**, 175 (2009) (in Chinese).
5. X.B. Chen and S.S. Mao, *Chem. Rev.,* **107**, 2891 (2007).
6. L.P. Huang, D.H. Chen, M.H. Huang and L. Chen, *Chin. J. Environ. Eng.,* **6**, 57 (2012) (in Chinese).
7. H.-S. Son, G. Ko and K.-D. Zoh, *J. Hazard. Mater.,* **166**, 954 (2009).
8. K. Elghniji, O. Hentati, N. Mlaik, A. Mahfoudh and M. Ksibi, *J. Environ. Sci.*, **24**, 479 (2012).
9. S.P. Kamble, S.B. Sawant and V.G. Pangarkar, *J. Hazard. Mater.*, **140**, 149 (2007).
10. D.L. Li, L. Zhang, X.J. Zhong and G.M. Li, *Chem. Online*, **8**, 577 (2006) in Chinese.
11. M. Sanchez, M.J. Rivero and I. Ortiz, *Appl. Catal. B: Environ.,* **101**, 515 (2011).
12. N. San, A. Hatipoglu, G. Koçtürk and Z. Çinar, *J. Photochem. Photobiol. A: Chem.,* **13**, 225 (2001).
13. B. Stoffler and G. Luft, *Chemosphere*, **38**, 1035 (1999).
14. T. Wu, X. Cai, S.Z. Tan, H. Li, J. Liu and W. Yang, *Chem. Eng. J.*, **173**, 144 (2011).
15. L. Zhang, D.L. Li, J.H. Cui and G.M. Li, *J. Instrum. Anal.*, **25**, 108 (2006) (in Chinese).
16. G.Z. Ji, Y. Zhang, X.Q. Zhang and F.F. Chu, *Phys. Chem. J. Nanjing Normal Univ.*, **9**, 52 (2009) (in Chinese).