EnvironmentAsia
The international journal published by the Thai Society of Higher Education Institutes on Environment

Available online at www.tshe.org/EA
EnvironmentAsia 1 (2009) 23-29

Photocatalytic Removal of Phenol under Natural Sunlight over N-TiO_2-SiO_2 Catalyst: The Effect of Nitrogen Composition in TiO_2-SiO_2

Viet-Cuong Nguyen [a] and The-Vinh Nguyen [b]

[a] *Binhdinh Department of Natural Resource and Environment, Quynhon city, Vietnam*
[b] *Faculty of Environment, Hochiminh City University of Technology, Hochiminh city, Vietnam*

Abstract

In this present work, high specific surface area and strong visible light absorption nitrogen doped TiO_2-SiO_2 photocatalyst was synthesized by using sol-gel coupled with hydrothermal treatment method. Nitrogen was found to improve the specific surface area while it also distorted the crystal phase of the resulting N-TiO_2-SiO_2 catalyst. As the N/(TiO_2-SiO_2) molar ratio was more than 10%, the derived catalyst presented the superior specific surface area up to 260 m^2/g. Nevertheless, its photoactivity towards phenol removal was observed to significantly decrease, which could results from the too low crystallinity. The nitrogen content in N-TiO_2-SiO_2 catalyst was therefore necessary to be optimized in terms of phenol removal efficiency and found at ca. 5%. Under UVA light and natural sunlight irradiation of 80 min, N(5%)-TiO_2-SiO_2 catalyst presented the phenol decomposition efficiencies of 68 and 100%, respectively. It was also interestingly found in this study that the reaction rate was successfully expressed using a Langmuir-Hinshelwood (L-H) model, indicating the L-H nature of photocatalytic phenol decomposition reaction on the N-TiO_2-SiO_2 catalyst.

***Keywords**:* nitrogen doped TiO_2-SiO_2; photocatalysis; phenol decomposition; natural sunlight; kinetics

1. Introduction

Owing to the coming energy crisis on the earth as well as the instability of oil price in recent years, various inter-discipline research groups have paid much attention to the field of renewable energy (Smalley, 2003). Direct utility of natural sunlight for clean energy production and for removal of pollutants in air, water and soils (Kaneko, 2002) seem to be fruitful over the last decades. Among a huge numbers of materials and methods that are commonly employed for the above research, photocatalysis has presented its miracle role in the field of environmental treatment (Fujishima *et al.*, 1999; Nguyen and Nguyen, 2007) and renewable energy (Smalley, 2003; Nguyen *et al.*, 2006).

TiO_2-based catalyst has been one of the key materials in photocatalysis since the first exploration of Fujishima and Honda was done on TiO_2 for photoelectrolysis of water to H_2 in 1972 (Fujishima and Honda, 1972). Although TiO_2 as a role of photocatalyst has been substantially commercialized for our daily life (Kaneko, 2002; Fujishima *et al.*, 1999), there is still much room for researchers in this field to further explore the improvement of photoactivity of TiO_2-based catalyst. Enhancement of the specific surface area as well as the visible light absorption ability of photocatalyst have been much paid attention by different groups for the aim of practical applications of TiO_2-based photocatalyst (Dutoit *et al.*, 1996; Gao and Wachs, 1999; Nguyen and Yang, 2003; Nguyen *et al.*, 2005; Nguyen and Yang, 2004).

In this present study, in order to increase the specific surface area of the TiO_2 photocatalyst and simultaneously extend its light absorption spectroscopy to visible range, nitrogen doped TiO_2-SiO_2 photocatalyst is synthesized by sol-gel coupled with hydrothermal treatment method. The photoactivity of the derived catalyst is tested by using a reaction of phenol decomposition under UV light and natural sunlight in Hochiminh city, Vietnam. The effect of content of nitrogen doped in TiO_2-SiO_2 on its photocatalytic activity towards phenol removal as well as the kinetics of the reaction are also studied and discussed.

2. Materials and Methods

The procedures of preparation of TiO_2-SiO_2 were mentioned in details in our previous study (Nguyen and Nguyen, 2007). Three solutions were first prepared: the first solution denoted as S1 was prepared by mixing solvents (a mixture of ethanol and iso-propanol with the volume ratio = 1:1) with water and nitric acid; the second one included the solvents, water and tetraethyl orthorsilicate (TEOS, Merck), which was strongly mixed in a beaker at ca. 300 rpm; the third solution was a mixture of the solvents and titanium (IV) isopropoxide (TTIP, Merck). The above three solutions were then mixed and refluxed at 80 °C for 1 h under vigorous stirring (*ca*. 1500 rpm). The obtained sol-gel solution was thereafter hydrothermally treated in a lab-made autoclave at 150 °C for 10 h. After that,

Table 1. Specific surface areas and the particle sizes (d_{XRD}) of various N-TiO_2-SiO_2 catalysts

Sample	S_{BET} (m^2/g)	XRD particle size [a] (d_{XRD}, nm)
N0	164.5	9.68
N5	172.36	9.88
N10	153.47	8.83
N50	225.05	7.00
N100	238.37	6.42
N150	264.24	6.31
N200	266.66	6.27

[a] XRD particle size was estimated by using the Scherer equation.

the solvents were removed at 50 °C using a rotary vacuum system. The aerogel was later dried in an oven at 105 °C for 2 h and then calcined at 550 °C.

For synthesis of N-TiO_2-SiO_2 catalyst, corresponding amount of urea was dissolved in the S1 solution to get the final urea/(TiO_2 + SiO_2) molar ratio of 0.05/1, 0.1/1, 0.5/1, 1/1, 1.5/1 and 2.0/1, whose corresponding derived catalysts are denoted as N5, N10, N50, N100, N150 and N200, respectively.

In both TiO_2-SiO_2 and N-TiO_2-SiO_2 mixed oxides, the TiO_2 : SiO_2 weight ratio was controlled at 95 : 5. The crystallinity of catalyst was measured by using X-ray diffraction (Rikagu, Cu K_α) . The BET specific surface area of catalyst was determined by nitrogen adsorption at -196 °C (Chembet 3000). The bandgap energy of catalyst was estimated by using UV-Vis diffuse reflectance spectroscopy (Jasco 500). The catalyst particle size and morphology were measured by using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800).

Photocatalytic decomposition of phenol was carried out in a 1 L reactor containing 300 ml of 10 ppm phenol aqueous solution and 0.15 g of catalyst. The reaction solution was well mixed by magnetic bar at *ca.* 200 rpm. The outer light source for the reaction consisted of two UVA lamps with the total capacity of 30 W and the peak of light spectrum at 365 nm. Before turning on the lamps, the reaction solution was well mixed for 30 min in dark to ensure the equilibrium processes of adsorption and desorption of phenol on the catalyst surface. For the analysis of phenol concentration after each period of 20 min, 5 ml of the solution was sampled, centrifuged (ca. 6000 rpm in 10 min) and filtered (using a 0.45 μm filter, Merck). The phenol concentration was determined by using UV-Vis spectroscopy (Cary Varian 50). The reactor temperature was maintained at around 30 °C using a water cooling system. For the experiment under natural sunlight, the reactor was left outdoor in a sunny day from 11:00 am to 13:00 pm in Hochiminh city. The sunlight intensity during the experiment time was estimated by using a lumen meter (Lux 5924, Hana).

3. Results and Discussion

3.1. Characterization of photocatalyst

Table 1 presents the effect of nitrogen content in N-TiO_2-SiO_2 catalyst on its specific surface area and XRD particle size that was estimated by using the Scherer equation. It was interestingly found that the S_{BET} of N-TiO_2-SiO_2 catalysts with the N : (TiO_2-SiO_2) molar ratio less than 50% were low and comparable with that of bare TiO_2-SiO_2. Nevertheless, when the N : (TiO_2-SiO_2) molar ratio was higher than 50%, the specific surface area of the resulted catalyst was observed to significantly increase. The results could be ascribed to the employment of urea as the precursor for nitrogen addition to TiO_2-SiO_2 catalyst. In the case of N : (TiO_2-SiO_2) molar ratio higher than 50%, the pH value of the N-TiO_2-SiO_2 sol-gel solution was observed to substantially increase. As the molar ratio of N : (TiO_2-SiO_2) reached a critical value, it could result in the superior precipitation of N-TiO_2-SiO_2 during the sol-gel process. This phenomenon could bring about the high specific surface area of the obtained N-TiO_2-SiO_2 catalyst with the N : (TiO_2-SiO_2) molar ratio higher than 50%.

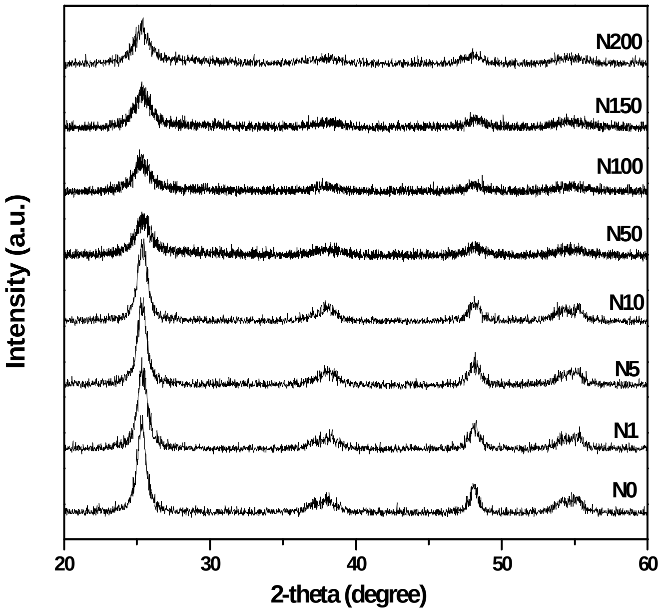

Figure 1. XRD patterns of different N-TiO_2-SiO_2 catalysts.

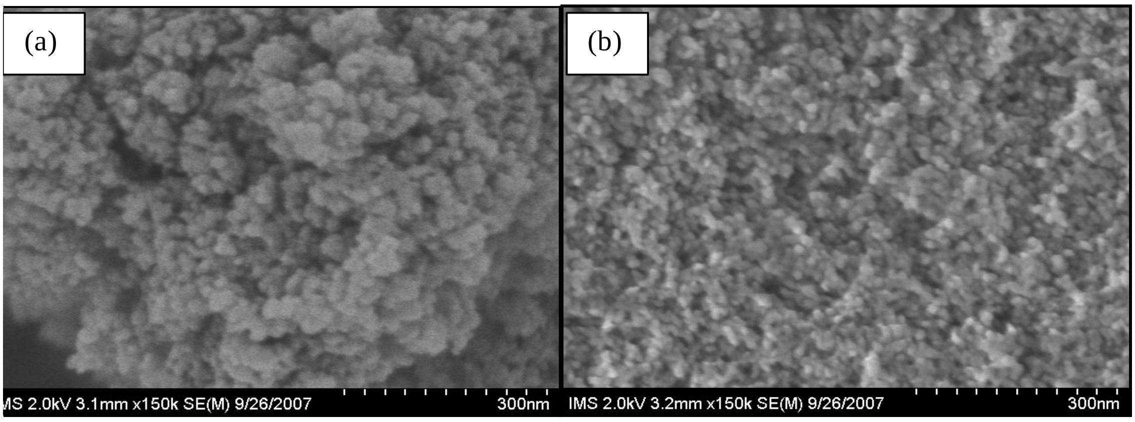

Figure 2. FE-SEM images of (a) TiO$_2$-SiO$_2$ and (b) N-TiO$_2$-SiO$_2$ catalysts.

X-ray diffraction patterns of different N-TiO$_2$-SiO$_2$ catalysts are shown in Fig. 1. Nitrogen was found to significantly decrease the crystallinity of derived N-TiO$_2$-SiO$_2$ catalyst in comparison with that of bare TiO-$_2$-SiO$_2$. When the molar ratio of N: (TiO$_2$-SiO$_2$) was higher than 50%, the crystallinity of N-TiO$_2$-SiO$_2$ catalyst was substantially decreased and much different from those with the (N : TiO$_2$-SiO$_2$) molar ratio less than 50%. It was well agreed that the higher the specific surface area, the lower the crystallinity of catalyst (Nguyen *et al.*, 2006). Accordingly, the X-ray diffraction results were well consistent with the specific surface area and the XRD particle size data as presented in Table 1.

Fig. 2 shows the morphology of TiO$_2$-SiO$_2$ and N-TiO$_2$-SiO$_2$ (N5) catalysts measured by field-emission scanning electron microscopy (FE-SEM). Based on the scale of the FE-SEM pictures in Fig. 2, the particle sizes of TiO$_2$-SiO$_2$ and N-TiO$_2$-SiO$_2$ (N5) were estimated at around 13 and 8.8 nm, respectively. It was obviously that nitrogen was observed to decrease the particle size and therefore, increase the specific surface area of the resulting N-TiO$_2$-SiO$_2$ catalyst. Conclusively, nitrogen was found to improve the specific surface area of the resulting N-TiO$_2$-SiO$_2$ catalyst while it was also observed to distort the crystal phase of the catalyst.

UV-Vis spectroscopies of different N-TiO$_2$-SiO$_2$ catalysts are depicted in Fig. 3. As TiO$_2$-SiO$_2$ was doped with nitrogen, the resulting catalysts were observed to shift to the visible range. Visible light shift was observed on all of the N-TiO$_2$-SiO$_2$ catalysts. When the N : (TiO$_2$-SiO$_2$) molar ratio was increased from 1 to 10%, the visible light absorption behavior of the derived N-TiO$_2$-SiO$_2$ catalyst was

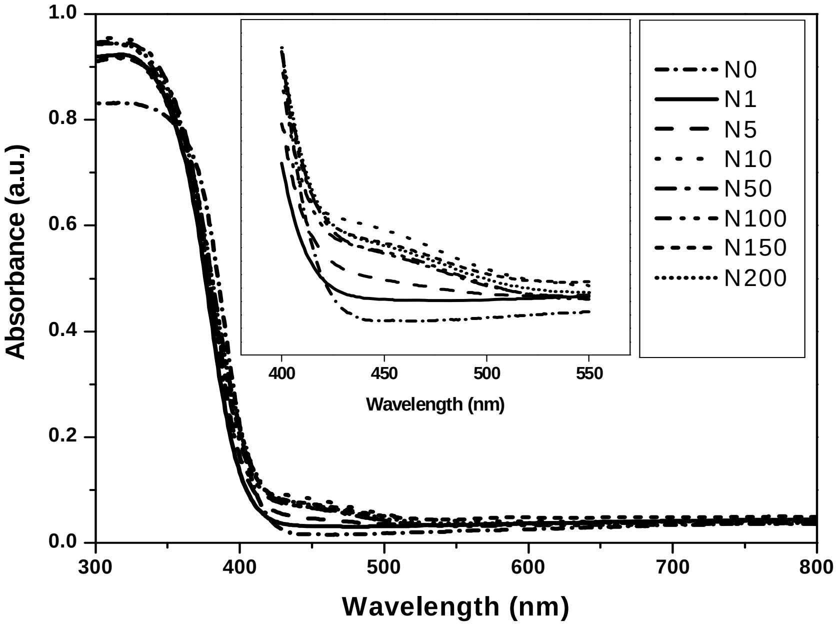

Figure 3. UV-Vis spectroscopies of different N-TiO$_2$-SiO$_2$ catalysts. The inset shows the large scale spectroscopies of the catalysts in the wavelength range of 400 – 550 nm.

found to gradually increase. N5 catalyst presented strong visible light absorption with one peak observed at the wavelength of around 462 nm. Nevertheless, as the N : (TiO_2-SiO_2) molar ratio was over 10%, the UV-Vis spectra of the resulting N-TiO_2-SiO_2 catalysts were found alike as shown in Fig. 3. These results implied that there existed a critical value of nitrogen content in N-TiO_2-SiO_2 catalyst to determine its red-shift property. As the content of nitrogen in N-TiO_2-SiO_2 catalyst was larger than the critical value, the remaining amount of nitrogen could be removed under calcination process instead of inserted into the TiO_2-SiO_2 lattice.

3.2. Photocatalytic decomposition of phenol over different N-TiO_2-SiO_2 catalysts under UVA light irradiation

Table 2 shows the decomposition efficiency of phenol over different N-TiO_2-SiO_2 catalysts under UVA light irradiation. In order to determine the adsorption efficiency of phenol on the catalyst surface, the reaction solution including N-TiO_2-SiO_2 catalyst and phenol aqueous solution was well mixed under dark for 30 min before turning on the lamps. The adsorption efficiency was found at between 5% and 12 %, which was relatively consistent with the specific surface area of the catalyst. The larger the specific surface area, the higher the efficiency of the catalyst towards phenol adsorption under dark. When the UVA light was turned on, decomposition of phenol over N-TiO_2-SiO_2 catalyst substantially increased as shown in Table 2. As compared to bare TiO_2-SiO_2, N-TiO_2-SiO_2 catalyst presented strong photocatalytic activity towards phenol removal with the efficiencies of 44 and 89%, respectively after 2 h of irradiation. Nevertheless, as the N : (TiO_2-SiO_2) molar ratio was over 5%, the phenol decomposition efficiency of the derived N-TiO_2-SiO_2 catalyst was significantly decreased. The efficiency of N200 catalyst towards phenol decomposition (32%) was even much lower than that of bare TiO_2-SiO_2 (44%).

Although the increase in the N : (TiO_2-SiO_2) molar ratio of more than 10% was found to significantly improve the specific surface area of the derived N-TiO_2-SiO_2 catalyst from 153 to 266 m^2/g, this positive effect was followed by the strong decline of the crystallinity of the catalysts as shown in Fig. 1. As discussed in the previous section, when the N : (TiO_2-SiO_2) molar ratio was more than 10%, it did not affect the band-gap energy but distorted the crystallinity of the resulting N-TiO_2-SiO_2 catalyst. Consequently, the best photoactitvity towards phenol removal was only observed on N-TiO_2-SiO_2 catalyst with the N : (TiO_2-SiO_2) molar ratio lower than 10%.

Study on the kinetics of the photocatalytic decomposition of phenol over different N-TiO_2-SiO_2 catalysts was also done in this present work. The half-life decomposition time ($t_{1/2}$) was also determined for simple comparison with other research data. The results are shown in Fig. 4.

According to the kinetic results shown in Fig. 4 and Table 3, it could be concluded that the reaction rate was successfully expressed using a Langmuir-Hinshelwood (L-H) model. In other words, the kinetic results indicated the L-H nature of photocatalytic phenol decomposition reaction on the N-TiO_2-SiO_2 catalyst under UVA irradiation.

It was also observed that N1 and N5 catalysts presented too high reaction rate coefficient k with

Table 2. Adsorption and decomposition efficiency of phenol over N-TiO-$_2$-SiO_2 with different nitrogen contents under UVA light irradiation

Catalyst	**Saturated adsorption efficiency (%) (30 min under dark)**	**Phenol removal efficiency (%) (120 min under UVA light irradiation)**
N0	5.0	44.2
N1	8.0	85.2
N5	5.6	88.9
N10	4.6	70.0
N50	8.8	48.3
N100	10.0	45.1
N150	12.2	35.3
N200	12.4	31.7

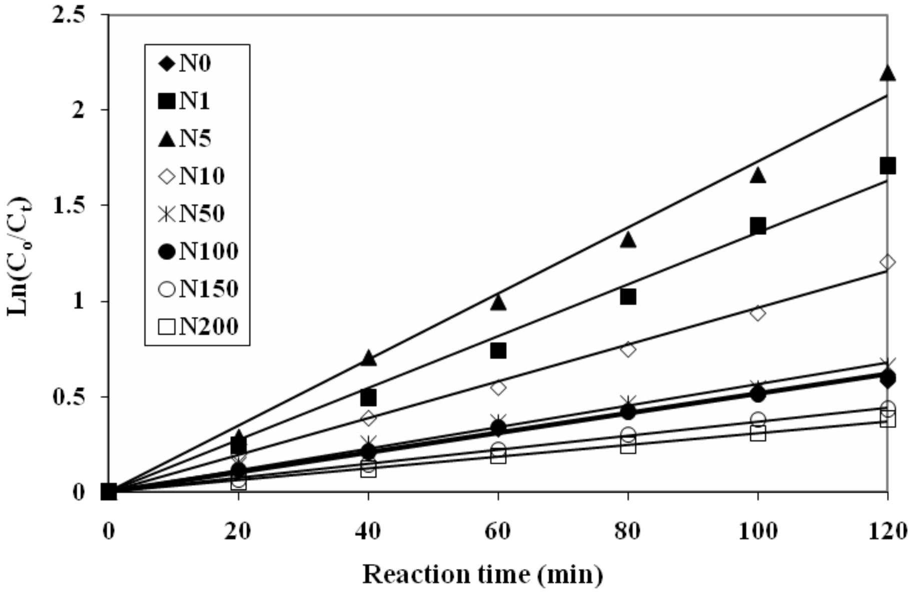

Figure 4. Ln(C_o/C_t) according to reaction time of different N-TiO_2-SiO_2 catalysts. C_o and C_t were the phenol concentrations at the initial and corresponding reaction time, respectively. The reaction was carried out under UVA irradiation with C_o = 10 mg/l and the amount of catalyst of 0.5g/L.

the values of 0.0136 and 0.0173 min^{-1}, respectively. These values were around 3 times higher than that of bare TiO_2-SiO_2 catalyst.

3.3. Photocatalytic decomposition of phenol over different N-TiO_2-SiO_2 catalysts under natural sunlight irradiation

For energy-saving purpose, the photocatalytic reaction of phenol decomposition was carried out by utilizing the abundant natural sunlight in Hochiminh city with the data shown in Fig. 5. It was interestingly found that under natural sunlight the N-TiO_2-SiO_2 catalysts presented strong photocatalytic activities towards phenol removal in comparison with the case of using UVA light as the irradiation source. The order of photoactivity of the catalysts was as follows: N5 > N10 > N100 > N0 > N200. Only after 80 min of natural sunlight irradiation, the phenol removal efficiency of 100% is observed on N5 catalyst. This superior photoactivity of N-TiO_2-SiO_2 catalyst could be ascribed to the strong intensity of the natural sunlight as compared to UVA light. The average intensity of the natural sunlight was estimated at around 1 sun or 100 mW/cm^2 that was much higher than the intensity of UVA light of around 15 mW/cm^2 in this present work. The result certainly presented potential application

Table 3. Kinetic parameters of phenol removal reaction over different N-TiO_2-SiO_2 catalysts under UVA irradiation

Sample	**Apparent reaction rate coefficient k (min^{-1})**	**Half-life decomposition time $t_{1/2}$ (min)**	**R^2**
N0	0.0052	133.27	0.9921
N1	0.0136	50.74	0.9912
N5	0.0173	40.06	0.9922
N10	0.0096	72.19	0.9956
N50	0.0056	123.75	0.9901
N100	0.0052	133.27	0.9947
N150	0.0037	187.30	0.9983
N200	0.0031	223.55	0.9977

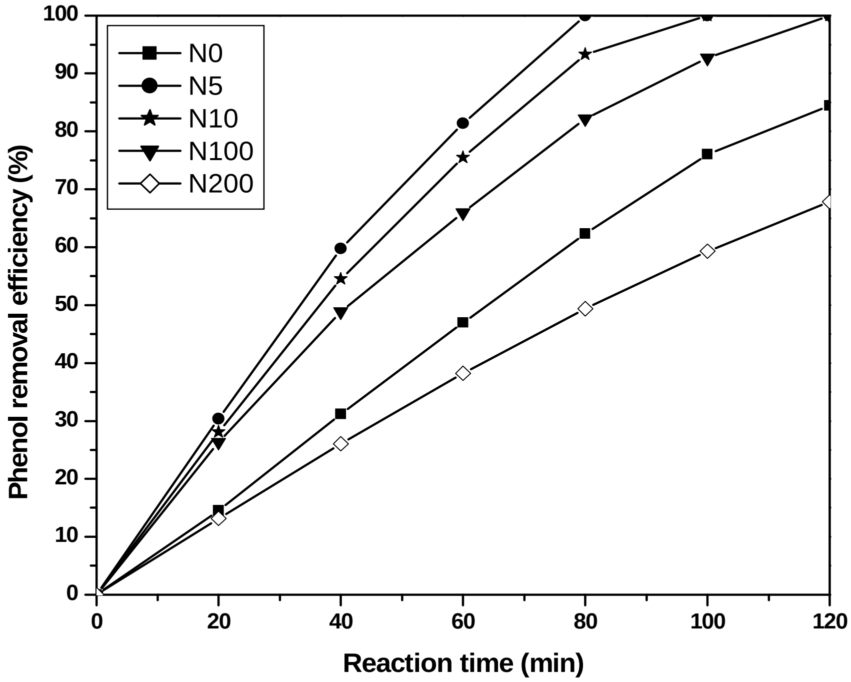

Figure 5. Phenol removal efficiency according to reaction time over different N-TiO_2-SiO_2 catalysts under natural sunlight irradiation.

of photocatalyst in Hochiminh city for environmental treatment.

4. Conclusions

The presence of nitrogen in N-TiO_2-SiO_2 catalyst was found to not only improve the specific surface area but also to shift the UV-Vis spectroscopy of the catalyst to visible range. Nevertheless, when the content of nitrogen in N-TiO_2-SiO_2 catalyst was higher than a critical value, it was observed to distort the crystallinity and therefore decrease the photocatalytic activity of the resulting catalyst. N(5wt%)-TiO_2-SiO_2 was found to be the best photocatalyst towards phenol removal under both UVA and natural sunlight irradiation with the efficiencies of 68 and 100%, respectively after 80 min of reaction. The reaction rate of photocatalytic phenol removal on N(5wt%)-TiO_2-SiO_2 catalyst was observed to be expressed using a Langmuir-Hinshelwood (L-H) model with k coefficient of 0.0173 min^{-1} which was over 3 times higher than that of bare TiO_2-SiO_2 counterpart.

Acknowledgements

The authors gratefully acknowledge the financial support from the Vietnam Ministry of Science and Technology through the Technological Incubation Program. We also thanks for the kind suggestions and helps of colleagues from the Faculty of Environment, Faculty of Materials Technology and Faculty of Chemical Technology, Hochiminh City University of Technology.

References

Dutoit DCM, Gobel U, Schneider M, Baiker A. Titania–Silica mixed oxides V. Effect of sol-gel and drying conditions on surface properties. Journal of Catalysis 1996; 164: 433-39.

Fujishima A, Hashimoto K, WatanabeT. TiO_2 Photocatalysis Fundamentals and Applications, BKC, Tokyo, Japan. 1999.

Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature 1972; 238: 37-38.

Gao X, Wachs IE. Titania–silica as catalysts: molecular structural characteristics and physico-chemical properties. Catalysis Today 1999; 51: 233-54.

Kaneko M, Okura I. Photocatalysis: Science and Technology. Springer, New York, USA. 2002.

Nguyen TV, Choi DJ, Yang OB. Effect of chelating agents on the properties of TiO_2-SiO_2 mixed oxide for photocatalytic water decomposition. Research on Chemical Intermediates 2005; 31: 483-91.

Nguyen TV, Lee HC, Yang OB. The effect of pre-thermal treatment of TiO_2 nanoparticles on the performance of dye-sensitized solar cells. Solar Energy Materials and Solar Cells 2006; 90: 967-81.

Nguyen TV, Yang OB. Photoresponse and AC impedance characterization of TiO_2-SiO_2 mixed oxide for photocatalytic water decomposition. Catalysis Today 2003; 87: 69-75.

Nguyen TV, Yang OB. Water decomposition on TiO_2-SiO_2 and RuS_2/TiO_2-SiO_2 photocatalysts: the effect of electronic characteristics. Catalysis Communications 2004; 5: 59-62.

Nguyen VC, Nguyen TV. Synthesis and characterization of N-TiO_2-SiO_2 photocatalyst for decomposition of phenol under natural sunlight. Proceedings of the First

International Workshop on Nanotechnology and Application 2007; 507-14.

Smalley RE. Our energy challenge. Energy & Nanotechnology Conference 2003. Rice University, Houston, USA, May 3, 2003.

Received 12 October 2008
Accepted 30 November 2008

Correspondence to
Dr. The-Vinh Nguyen
Faculty of Environment,
Hochiminh City University of Technology,
Hochiminh city,
Vietnam
Email address: ntvinh@hcmut.edu.vn (T.-V. Nguyen).
Fax: +84 8 8639 682
Tel. : +84 8 8639 682