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Journal of Experimental Nanoscience

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t716100757>

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To cite this Article Nguyen, Viet-Cuong and Nguyen, The-Vinh(2009) 'Photocatalytic decomposition of phenol over N-TiO₂-SiO₂ catalyst under natural sunlight', Journal of Experimental Nanoscience, 4: 3, 233 – 242

To link to this Article: DOI: 10.1080/17458080902773707

URL: <http://dx.doi.org/10.1080/17458080902773707>

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Photocatalytic decomposition of phenol over N–TiO₂–SiO₂ catalyst under natural sunlight

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(Received 26 April 2008; final version received 23 January 2009)

Gel-derived TiO₂–SiO₂ and N–TiO₂–SiO₂ mixed oxides with the TiO₂:SiO₂ weight ratio of 95:5 are synthesised and employed for phenol removal under UVA light and natural sunlight in this study. Both SiO₂ and N are interestingly found to improve the specific surface area of resulting catalysts up to 169 m² g⁻¹. Meanwhile, only N is observed to shift significantly the light absorption of derived catalyst to visible range. Optimisation between specific surface area and crystallinity in TiO₂–SiO₂ mixed oxide is found to give rise to the superior photoactivity of TiO₂–SiO₂ catalyst in comparison with TiO₂ counterpart. Under natural sunlight in Hochiminh City on October 2007, N–TiO₂–SiO₂ presents the outstanding photoactivity towards decomposition of 10 ppm phenol aqueous solution with the efficiency up to 100% as compared to those of 65 and 48% for bare TiO₂–SiO₂ and bare TiO₂, respectively.

Keywords: N–TiO₂–SiO₂ mixed oxide; high specific surface area; phenol removal; natural sunlight

1. Introduction

Since the first exploration of Fujishima and Honda on TiO₂ for photoelectrolysis of water to H₂ [1], TiO₂ material has been intensively and extensively studied in various kinds of fields owing to its miracle properties [2]. In order to enhance the activity of TiO₂ catalyst, much attention has been paid by many research groups to the increase in its specific surface area by atomic mixing of SiO₂ with TiO₂ [3–7]. Nevertheless, as SiO₂ is inserted in TiO₂ lattice, the improvement of specific surface area of the resulting catalyst is also accompanied by the broadening of its bandgap energy [4]. As a consequence, TiO₂–SiO₂ mixed oxide inherently absorbs much more UV light than visible counterpart compared to bare TiO₂.

Although nitrogen-doped TiO₂ (N–TiO₂) catalyst has been intensively studied for the absorption of visible light [8–12], nitrogen-doped TiO₂–SiO₂ (N–TiO₂–SiO₂) catalyst has not been much explored. In this present research, the N–TiO₂–SiO₂ mixed oxide is

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synthesised using the sol-gel method. For simultaneous improvement of the specific surface area and crystallinity of N-TiO₂-SiO₂ catalyst, hydrothermal treatment is also employed right after the sol-gel process. The derived catalysts are characterised by using nitrogen adsorption for BET specific surface area, X-ray diffraction for crystallinity, UV-vis spectroscopy for light absorption and field-emission scanning electron microscopy (FE-SEM) for morphology. The photoactivities of catalysts are tested in the decomposition reaction of phenol in aqueous solution under UVA light and natural sunlight irradiation.

2. Experimental

2.1. Catalyst preparation

Figure 1 shows the schematic diagram of the preparation of TiO₂-SiO₂ mixed oxide. 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 HCl; the second one denoted as S2 included the solvents, water and tetraethyl orthosilicate (TEOS, Merck), which was strongly mixed in a beaker; the third solution denoted as S3 was a mixture of the solvents and titanium(IV) isopropoxide (TTIP, Merck). The volume of the solvents in S1, S2 and S3 were 120, 60 and 60 mL, respectively. The corresponding amount of TEOS and TTIP were employed to obtain the final weight ratio of TiO₂:SiO₂ of 95:5. The molar ratios of H₂O:TEOS in S2 and H₂O:(TEOS + TTIP) in this experiment were 2:1 and 4:1, respectively. The corresponding amount of 35% HCl solution was used in S1 to control the pH of this solution at 1. 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, the solvents were removed at 50°C using a rotary

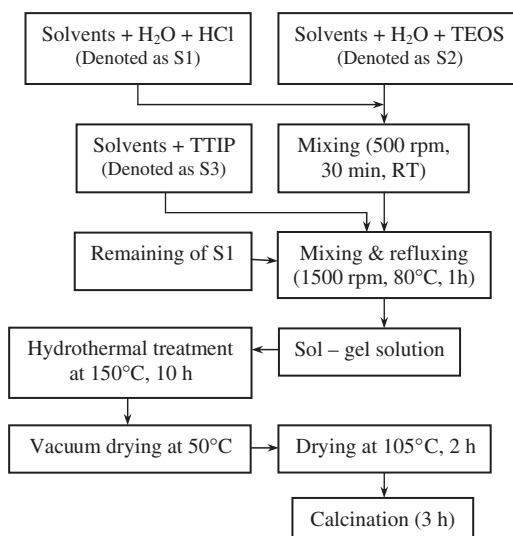


Figure 1. Schematic diagram of TiO₂-SiO₂ mixed oxide preparation.

vacuum system. The aerogel was later dried in an oven at 105°C for 2 h and then calcined at different temperatures.

For the synthesis of N-TiO₂-SiO₂ catalyst, corresponding amount of urea was dissolved in the S1 solution to get the final urea:(TiO₂+SiO₂) molar ratio of 1:1. Hydrochloride acid in the S1 solution was replaced by nitric acid.

In both TiO₂-SiO₂ and N-TiO₂-SiO₂ mixed oxides, the TiO₂:SiO₂ weight ratio was controlled at 95:5. Calcination of catalyst was carried out at temperatures of 350°C, 400°C, 450°C, 500°C, 550°C, 600°C, 700°C and 900°C.

2.2. Catalyst characterisation and photocatalytic decomposition of phenol

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 77 K (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 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 *c.* 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 surface of catalyst. For the analysis of phenol concentration after each period of 20 min, 5 mL of solution was sampled, centrifuged (*c.* 6000 rpm in 10 min) and filtered (using a 0.45 μ m filter, Merck). The phenol concentration was determined by using UV-vis spectroscopy (Cary Varian 50). The reactor temperature was maintained at \sim 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 measured by using a lumen metre (Lux 5924, Hana).

3. Results and discussion

Table 1 presents the specific surface areas of different catalysts. It is found that lab-made TiO₂ prepared with sol-gel method and hydrothermal treatment shows very high BET specific surface area as compared with commercial TiO₂ (P25). As SiO₂ is atomically mixed with TiO₂, the specific surface area of resulting TiO₂-SiO₂ mixed oxide is significantly increased up to 143.5 m² g⁻¹. This value is around three times higher than that of bare TiO₂ catalyst. When nitrogen is doped in the TiO₂-SiO₂ material, the resulting N-TiO₂-SiO₂ is then observed to significantly increase up to 229.8 m² g⁻¹ on N-TiO₂-SiO₂-400 catalyst. Calcination temperature is found to strongly influence the specific surface area of N-TiO₂-SiO₂ catalyst as shown in Table 1. At low-calcination temperatures, from 350°C to 450°C, the specific surface area of N-TiO₂-SiO₂ is observed to increase and then decrease with the maximum value of 229.8 m² g⁻¹ at 400°C. This result may be ascribed to the contribution of remaining organic and inorganic compounds at low-calcination temperatures to the S_{BET} of the resulting catalysts. Calcination at 400°C may maximise the

Table 1. BET specific surface areas of different catalysts.

Catalyst	TiO ₂ :SiO ₂ weight ratio	S_{BET} (m ² g ⁻¹)
TiO ₂ (P25)	100:0	53.1
TiO ₂	100:0	82.7
TiO ₂ -SiO ₂	95:5	143.5
N-TiO ₂ -SiO ₂ -350	95:5	198.7
N-TiO ₂ -SiO ₂ -400	95:5	229.8
N-TiO ₂ -SiO ₂ -450	95:5	124.4
N-TiO ₂ -SiO ₂ -500	95:5	145.7
N-TiO ₂ -SiO ₂ -550	95:5	165.7
N-TiO ₂ -SiO ₂ -600	95:5	133.2
N-TiO ₂ -SiO ₂ -700	95:5	130.4
N-TiO ₂ -SiO ₂ -900	95:5	56.4

S_{BET} of both remaining organic and inorganic compounds in the N-TiO₂-SiO₂ catalyst. As calcination temperature increases from 450°C to 550°C, the S_{BET} of N-TiO₂-SiO₂ is observed to again increase and then reach the highest value of 165.7 m² g⁻¹ at 550°C. At these calcination temperatures, the remaining organic compounds in the catalyst could be completely removed, which in turn significantly produces a large number of micro-pores in the catalyst. As a consequence, the S_{BET} of catalyst calcined at 450–550°C is observed to increase. As calcination temperature is increased from 550°C to 900°C, the S_{BET} of N-TiO₂-SiO₂ is substantially decreased. It is well known that low-calcination temperature is followed by low crystallinity of the derived catalyst [13], which could be consistently observed in Figure 3(A). The lower the crystallinity, the higher is the BET specific surface area of catalyst [13]. When calcination temperature is increased to over 450°C for complete removal of organic compounds, the S_{BET} of catalyst is certainly improved. However, as the calcination temperature is too high, sintering effect is the main factor to increase the catalyst crystallinity, and therefore decrease its specific surface area [13].

Figure 2 presents the FE-SEM morphology of different catalysts. Bare TiO₂ catalyst depicts the largest particle size of around 30 nm. Meanwhile, when TiO₂ is doped with SiO₂ and nitrogen, the particle sizes of resulting catalysts are observed to significantly decrease as shown in Figure 2(a) and (c). The particle sizes of TiO₂-SiO₂ and N-TiO₂-SiO₂ catalysts are estimated around 13 and 8 nm, respectively.

X-ray diffraction patterns of nitrogen-doped TiO₂-SiO₂ mixed oxides calcined at different temperatures are shown in Figure 3(A). When calcination temperature is increased from 350°C to 900°C, the crystallinity of the catalyst is significantly improved. Figure 3(B) shows the X-ray diffraction patterns of TiO₂-SiO₂ and N-TiO₂-SiO₂ mixed oxides in comparison with those of bare lab-made TiO₂ and TiO₂-P25. Lab-made catalysts present only anatase phase, whereas both anatase and rutile phase are observed on TiO₂-P25. Crystal phase transformation is not observed on either bare TiO₂-SiO₂ or N-TiO₂-SiO₂. Meanwhile, on increasing calcination temperature to 900°C, phase transformation from anatase to rutile is found on TiO₂-P25 [13]. Thermal stability of TiO₂-SiO₂ and N-TiO₂-SiO₂ could result from the hydrothermal treatment process of sol-gel solution.

UV-vis DRS of N-TiO₂-SiO₂ mixed oxide calcined at different temperatures is shown in Figure 4. At low-calcination temperature, N-TiO₂-SiO₂ presents strong absorption of visible light. This result could be explained by the trace residue of organic compounds after

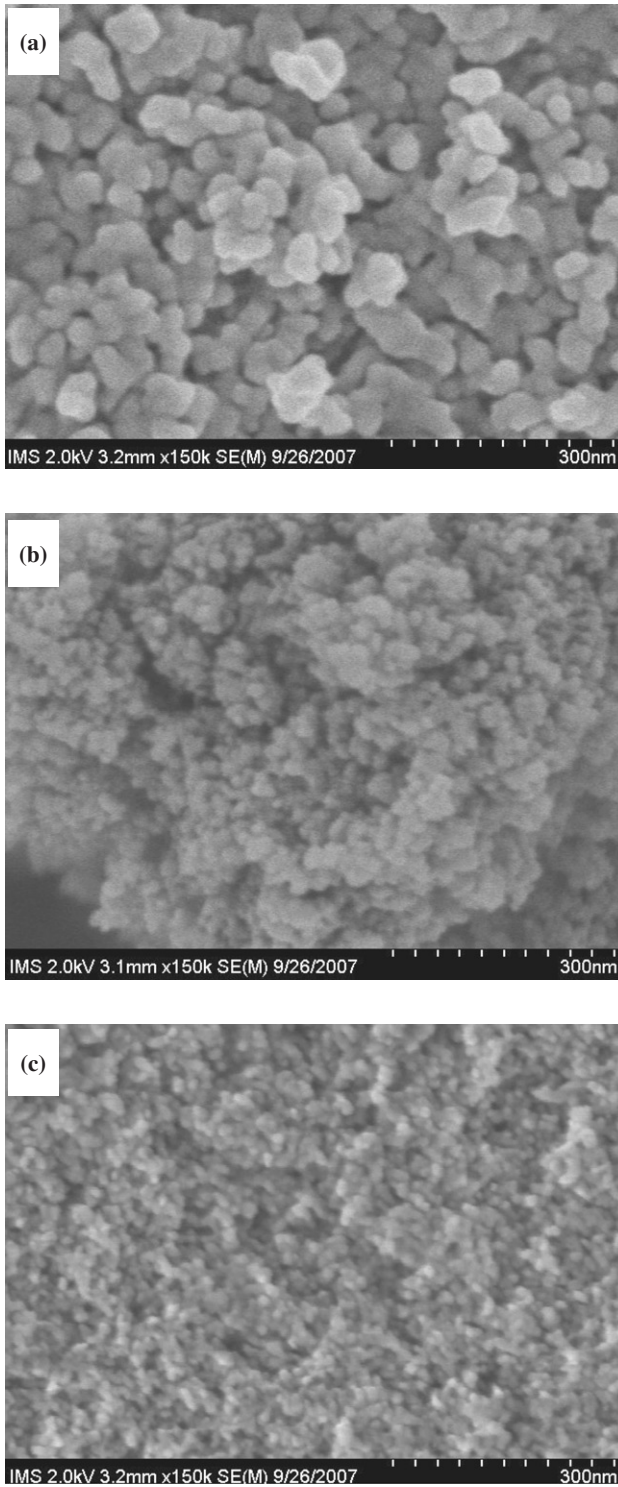


Figure 2. FE-SEM images of different catalysts. (a) TiO₂; (b) TiO₂-SiO₂ and (c) N-TiO₂-SiO₂.

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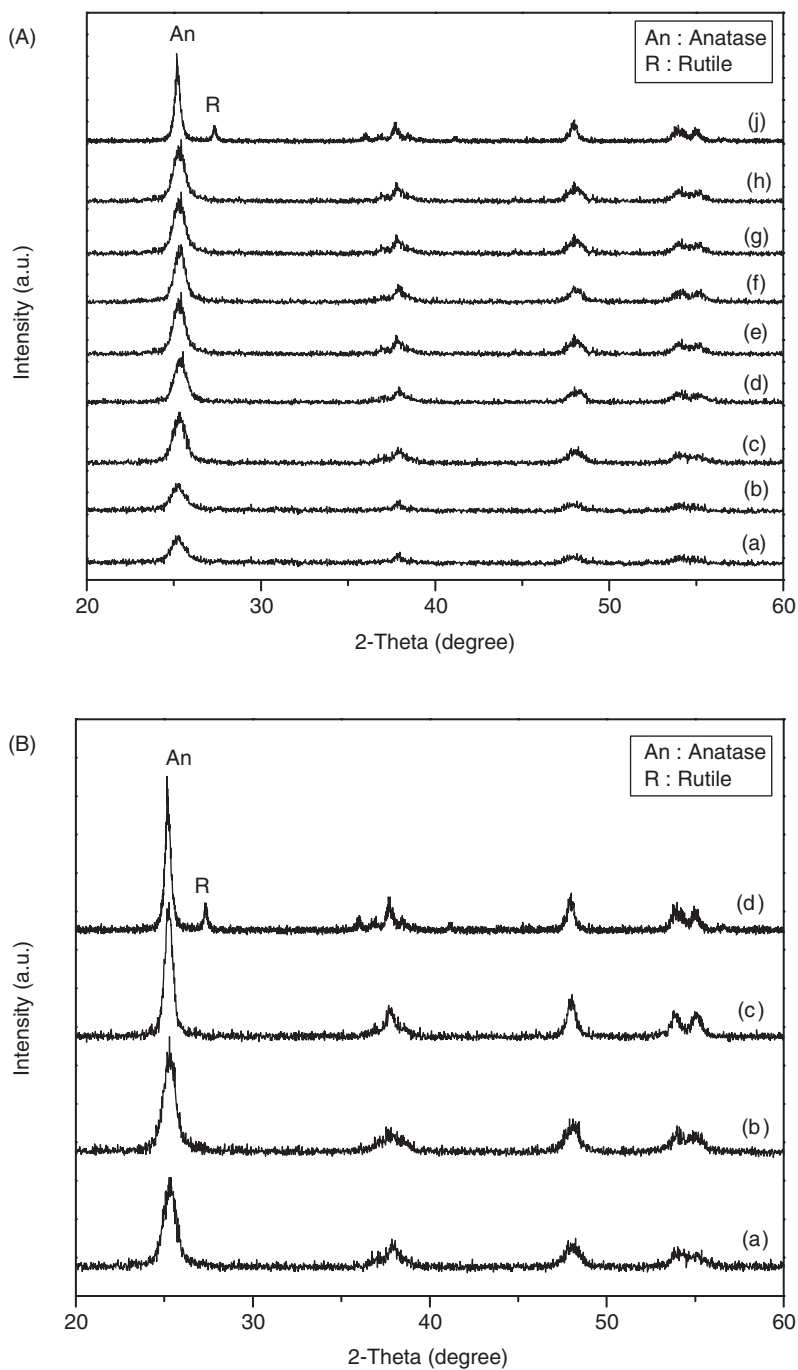


Figure 3. (A) XRD patterns of N-TiO₂-SiO₂ calcined at different temperatures: (a) 350°C, (b) 400°C, (c) 450°C, (d) 500°C, (e) 550°C, (f) 600°C, (g) 700°C, (h) 900°C and (j) TiO₂ (P25-Degussa); (B) XRD patterns of different catalyst: (a) N-TiO₂-SiO₂-550, (b) TiO₂-SiO₂-550, (c) TiO₂-550 and (d) TiO₂ (P25-Degussa).

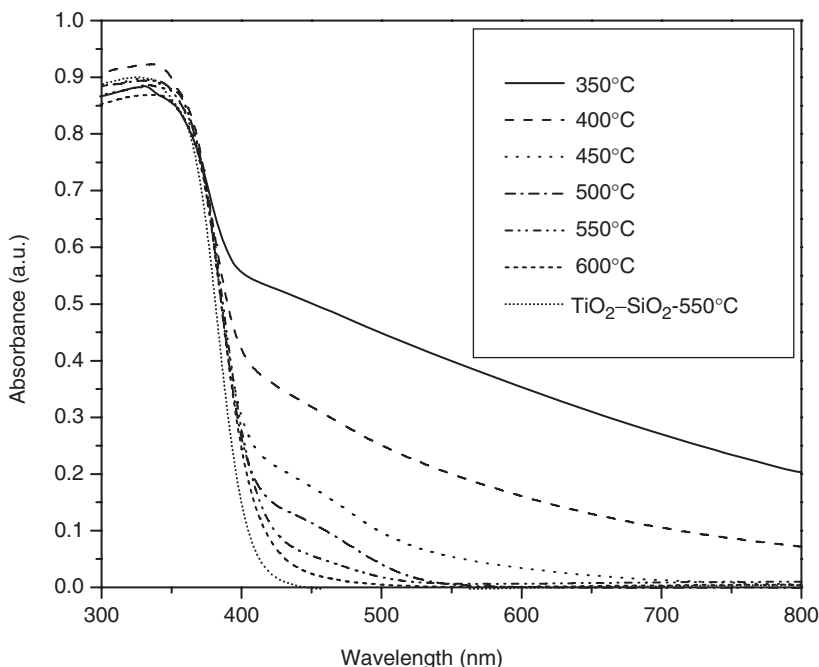


Figure 4. UV-vis DRS of N-TiO₂-SiO₂ mixed oxide calcined at different temperatures.

calcination of catalyst at low temperature. The colours of catalysts calcined at 350°C, 400°C and 450°C are observed by unaided eyes as brown, pale yellow and white, respectively. As increasing calcination temperature up to 500°C is well agreed to completely remove organic compounds, N-TiO₂-SiO₂ is still observed to have strong absorption of visible light as compared to bare TiO₂-SiO₂. This phenomenon is ascribed to the substitution of the oxygen atom in TiO₂-SiO₂ by its nitrogen counterpart [8,9], which results in the decrease in bandgap energy of the derived N-TiO₂-SiO₂ catalyst. As a consequence, the UV-vis spectrum of N-TiO₂-SiO₂ shifts to the visible range as shown in Figure 4.

Photocatalytic activities of different catalysts towards phenol removal under UVA light are shown in Table 2. As N-TiO₂-SiO₂ catalyst is calcined at temperatures lower than 450°C, its photoactivity efficiency is too low and comparable at ~20%. On increasing calcination temperature up to 450°C, phenol removal efficiency of catalyst is significantly improved from *c.* 20% to over 40% as presented in Table 2. The photoactivity of catalyst is then observed to increase to the maximum value at calcination temperature of 600°C. However, as the catalyst is calcined at temperature more than 600°C, its phenol removal efficiency is substantially reduced.

Although N-TiO₂-SiO₂-350 and N-TiO₂-SiO₂-400 catalysts present superior specific surface area and visible light absorption as shown in Table 1 and Figure 4, their crystallinity is too low because of a lot of organic traces in the catalyst. As a consequence, N-TiO₂-SiO₂-350 and N-TiO₂-SiO₂-400 catalysts display too low photoactivity towards phenol removal, which is ascribed to the large presence of recombination centres of excited electrons and holes in their lattices [14]. As calcination temperature is increased, the

Table 2. Phenol removal efficiency of different catalysts under UVA irradiation.

Catalysts	Phenol removal efficiency (%)
TiO ₂ -SiO ₂ -550	39.72 ± 1.6
N-TiO ₂ -SiO ₂ -350	16.49 ± 0.4
N-TiO ₂ -SiO ₂ -400	20.64 ± 0.5
N-TiO ₂ -SiO ₂ -450	41.10 ± 1.2
N-TiO ₂ -SiO ₂ -500	46.40 ± 1.4
N-TiO ₂ -SiO ₂ -550	49.48 ± 1.6
N-TiO ₂ -SiO ₂ -600	56.03 ± 1.7
N-TiO ₂ -SiO ₂ -700	40.41 ± 1.6
N-TiO ₂ -SiO ₂ -900	27.91 ± 1.1

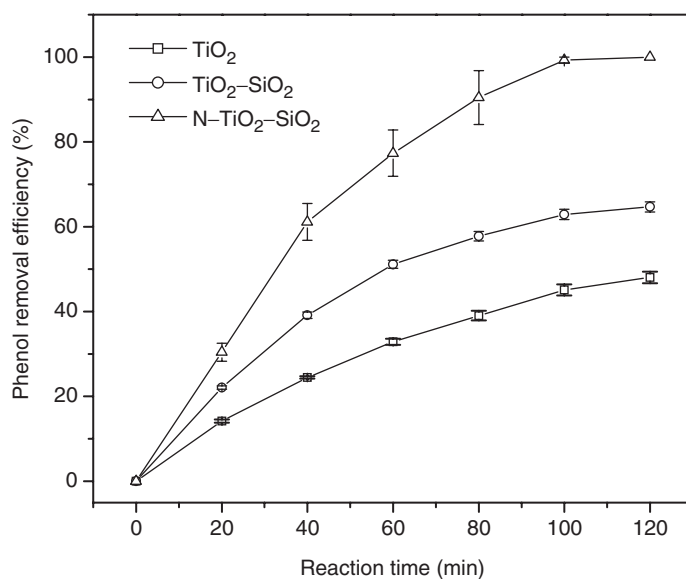


Figure 5. Phenol removal efficiency of different catalysts according to time under natural sunlight. The experiment was carried out outdoor in Hochiminh city from 11:00 am to 13:00 pm on 17 September, 2007 with the average light intensity of 80 klux.

regularity of catalyst lattice is gradually improved as presented in Figure 3(A). Nevertheless, the BET specific surface area and visible light absorption of the catalyst are largely weighed off (Table 1 and Figure 4). Accordingly, the optimum value of calcination temperature of catalyst inherently exists to obtain the best catalyst, that is, N-TiO₂-SiO₂-600 with the maximum phenol removal efficiency of 56.03%. It is also found in this study that the N-TiO₂-SiO₂ catalyst shows superior photoactivity towards phenol removal as compared to the bare TiO₂-SiO₂ counterpart under the same preparation condition.

Figure 5 depicts the phenol removal efficiency of different catalysts according to time under natural sunlight. It is interestingly found that N-TiO₂-SiO₂ presents superior

photoactivity towards phenol removal as compared to bare TiO_2 and $\text{TiO}_2\text{-SiO}_2$ catalysts. Although phenol removal efficiency of the $\text{N-TiO}_2\text{-SiO}_2$ catalyst is around 10% higher than that of the bare $\text{TiO}_2\text{-SiO}_2$ counterpart under UVA light irradiation, the photoactivity of the former towards phenol removal is up to 40% higher than that of the latter under natural sunlight irradiation. These results could be explained by the strongly visible absorption of $\text{N-TiO}_2\text{-SiO}_2$ in comparison with bare TiO_2 and $\text{TiO}_2\text{-SiO}_2$ as shown in Figure 4 as well as the superior specific surface area of the $\text{N-TiO}_2\text{-SiO}_2$.

4. Conclusions

The $\text{N-TiO}_2\text{-SiO}_2$ photocatalyst with high specific surface area and strong visible light absorption is synthesised and characterised for decomposition of phenol in aqueous solution. SiO_2 is found to significantly increase the specific surface area of the resulting $\text{TiO}_2\text{-SiO}_2$ mixed oxide. Meanwhile, the insertion of nitrogen in the $\text{TiO}_2\text{-SiO}_2$ lattice is observed to substantially shift the UV-vis spectroscopy of the derived $\text{N-TiO}_2\text{-SiO}_2$ to visible range. The high specific surface area up to $169\text{ m}^2\text{ g}^{-1}$ and good crystallinity of $\text{N-TiO}_2\text{-SiO}_2$ could also be ascribed to the hydrothermal treatment method that was employed right after the sol-gel process. Owing to strong absorption of visible light, high specific surface area and good crystallinity of the $\text{N-TiO}_2\text{-SiO}_2$ catalyst, its photoactivity towards phenol removal is superior compared to those of bare $\text{TiO}_2\text{-SiO}_2$ and the bare TiO_2 counterparts. The phenol removal efficiencies of $\text{N-TiO}_2\text{-SiO}_2$, $\text{TiO}_2\text{-SiO}_2$ and TiO_2 catalysts under natural sunlight in Hochiminh City in October 2007 are 100, 65 and 48%, respectively. The result presents strongly the potential application of $\text{N-TiO}_2\text{-SiO}_2$ in environmental treatment under real sunlight.

Acknowledgements

The authors gratefully acknowledge financial support from the Ministry of Science and Technology through the Technological Incubation programme. We also thank for their kind suggestions and help colleagues from the Faculty of Environment, the Faculty of Materials Technology and the Faculty of Chemical Technology, Hochiminh City University of Technology.

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