



## NO reduction and N<sub>2</sub> selectivity under various operating conditions for photo-SCR of NO

Yiang-Chen Chou, Young Ku\*

Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 106, Taiwan

### ARTICLE INFO

#### Article history:

Received 9 February 2010

Received in revised form 14 June 2010

Accepted 23 June 2010

#### Keywords:

Photo-SCR

Photocatalysis

NO reduction

Titanium dioxide

Eley–Rideal mechanism

### ABSTRACT

Photoassisted selective catalytic reduction (photo-SCR) of NO with ammonia under various operating conditions was investigated with a TiO<sub>2</sub>-coated annular photoreactor at room temperature. Effects of UV irradiance, inlet concentrations of O<sub>2</sub>, NO, NH<sub>3</sub> and H<sub>2</sub>O, and retention time of inlet stream on the NO reduction efficiency and N<sub>2</sub> selectivity were discussed in this study. The experimental results indicated that more than 70% of NO molecules could be reduced by photo-SCR with the retention time more than 4 min. N<sub>2</sub> selectivity was found to be decreased due to the generation of NO<sub>2</sub> and N<sub>2</sub>O molecules in the photo-SCR with specific operating conditions. Both NO reduction efficiency and N<sub>2</sub> selectivity were decreased for NO reduction by the photo-SCR with the presence of water molecules because of the competitive adsorption of water and NH<sub>3</sub> molecules on the active sites of TiO<sub>2</sub>. The reaction behavior of the NO reduction by the photo-SCR was adequately described by Eley–Rideal kinetics.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) such as nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), and nitrous oxide (N<sub>2</sub>O) exhausted from stationary emission source are considered as air contaminants due to the causative effects of town smog and acid rain. Selectively catalytic reduction (SCR) with ammonia has been widely applied to convert NO<sub>x</sub> emission into nitrogen and water at the operating temperature higher than 300 °C [1,2]. Numerous researchers focused their study on developing new techniques for operating SCR at lower temperature in order to conserve energy. Metal oxides deposited on supporting materials have been considered as advanced catalysts capable to be activated at low temperature. Huang et al. [3] prepared carbon nanotube supported vanadium oxide (V<sub>2</sub>O<sub>5</sub>/CNT) by an incipient wetness method and indicated that V<sub>2</sub>O<sub>5</sub>/CNT showed good reaction activity in NO reduction by the SCR with a temperature range of 100–250 °C.

Photoassisted selective catalytic reduction (photo-SCR) of NO with ammonia using semiconductor catalyst under appropriate illumination was regarded as another potential alternative for NO reduction at lower temperature [4]. Tanaka et al. [5] reported that NO reduction by the photo-SCR with ammonia over TiO<sub>2</sub> in the presence of oxygen could be operated at 50 °C. Photoirradiation of UV light caused remarkable enhancement of NO reduction to

form N<sub>2</sub>. The authors also indicated that NO molecules were weakly adsorbed on the active sites of TiO<sub>2</sub> as compared to NH<sub>3</sub> molecules. The formation of N<sub>2</sub> in the photo-SCR was consisted of one N atom derived from NH<sub>3</sub> and another N atom derived from NO.

Teramura et al. [6] applied FT-IR to measure the adsorbed species and intermediates derived from NO, NH<sub>3</sub> and O<sub>2</sub> on the surface of TiO<sub>2</sub> for investigating the reaction mechanism of NO reduction by the photo-SCR. NH<sub>3</sub> was found to be firstly adsorbed on the active sites of TiO<sub>2</sub> (Ti<sup>4+</sup>) and reacted with the light-induced holes to form NH<sub>2</sub> radicals. The formed NH<sub>2</sub> radicals reacted with NO in gas phase to form nitrosamide (NH<sub>2</sub>NO). The formation of N<sub>2</sub> and H<sub>2</sub>O was observed by the decomposition of NH<sub>2</sub>NO intermediate. Finally, the reduced active sites of TiO<sub>2</sub> (Ti<sup>3+</sup>) were re-oxidized to the original state (Ti<sup>4+</sup>) by O<sub>2</sub>. Teramura et al. [7] proposed the kinetic model of NO reduction in the photo-SCR according to Eley–Rideal mechanism and indicated that the rate-determining step was the decomposition of NH<sub>2</sub>NO for cases containing excessive O<sub>2</sub> and the re-oxidation of Ti<sup>3+</sup> for cases with insufficient O<sub>2</sub>. Yamazoe et al. [8] studied the effect of TiO<sub>2</sub> characteristics on the performance of NO reduction by the photo-SCR. The experimental results revealed that the reaction activity of photo-SCR was correlated to the amount of Lewis acid sites on the surface of TiO<sub>2</sub>, but was independent of specific surface area and crystal diameter of TiO<sub>2</sub>.

Since the NO reduction by the photo-SCR is significantly affected by the operating conditions, the most important course in this process is how to enhance the NO reduction efficiency and the N<sub>2</sub> selectivity. In this study, gaseous NO was reduced by photo-SCR

\* Corresponding author. Tel.: +886 2 27333141x7606; fax: +886 2 23785535.  
E-mail address: [ku508@mail.ntust.edu.tw](mailto:ku508@mail.ntust.edu.tw) (Y. Ku).

### Nomenclature

$C_{H_2O}$	the concentration of water [ppmv]
$C_{N_2}$	the concentration of nitrogen [ppmv]
$C_{NO,0}$	the inlet concentration of nitric oxide [ppmv]
$C_{NO}$	the concentration of nitric oxide [ppmv]
$C_{NO_2}$	the concentration of nitric dioxide [ppmv]
$C_{N_2O}$	the concentration of nitrous oxide [ppmv]
$C_{NH_3,0}$	the inlet concentration of ammonia [ppmv]
$C_{NH_3}$	the concentration of ammonia [ppmv]
$C_{O_2}$	the inlet concentration of oxygen [vol.%]
$E$	the reduction efficiency of NO (defined as the ratio of reduced NO concentration to the original concentration of NO) [%]
$I$	the irradiance of light source [ $mW/cm^2$ ]
$k_a$	the apparent reaction rate constant of NO reduction [ $(mW/cm^2)^{-n}/ppmv/min$ ]
$K$	the adsorption constant of ammonia [1/ppmv]
$K_s$	the surface reaction equilibrium constant [1/ppmv]
$K^*$	the adsorption constant of water [1/ppmv]
$n$	the reaction order against UV irradiance
RH	the relative humidity of system [%]
$r_{NO}$	the photocatalytic reduction rate of NO in the photo-SCR [ppmv/min]
$S$	the $N_2$ selectivity (defined as the ratio of $N_2$ concentration to the sum concentration of $N_2$ , $NO_2$ , and $N_2O$ at the outlet stream of photoreactor) [%]
$U$	the energy per mole photons at the wavelength of 365 nm [ $U_{365} = 3.28 \times 10^5 J/mol$ ]
$V$	the effective volume of photoreactor [ $cm^3$ ]
<i>Greek letters</i>	
$\tau$	the retention time of inlet stream [min]
$\phi_{NO}$	the apparent quantum yields of NO reduction
$\omega$	the wavelength of light source [nm]

with  $NH_3$  at room temperature in a  $TiO_2$ -coated annular photoreactor. NO reduction efficiency and  $N_2$  selectivity were determined from gases composition at the outlet stream of photoreactor. Effects of operating conditions, such as UV irradiance, inlet concentrations

of  $O_2$ , NO,  $NH_3$  and  $H_2O$ , and retention time of inlet stream, on the reduction behavior of NO by photo-SCR were investigated. A simplified kinetic model was established to express NO reduction by the photo-SCR with ammonia over  $TiO_2$  at room temperature based on Eley–Rideal mechanism.

## 2. Materials and methods

Titanium dioxide powder (P-25), a mixture of anatase and rutile, purchased from *Degussa* was used as the photocatalyst in this study. The suspension containing  $TiO_2$  weight percentage of 10% was prepared by adding 50 g  $TiO_2$  into 450 g of ethanol solution. The mixed solution was stirred with a mechanical stirrer for 2 h, and was then put in a sonicator for well mixing for more than 8 h. A quartz tube was dipped in the  $TiO_2$  suspension for 1 min before it was taken out and then dried at the room temperature. This coating procedure was repeated several times to increase the amount of  $TiO_2$  coated on the surface of quartz tube. The  $TiO_2$ -coated quartz tube was then put in the muffle furnace at  $350^\circ C$  for 1 h.

The schematic diagram of the photo-SCR system used in this study is shown in Fig. 1. The photocatalytic reaction was carried out in an annular reactor composed of the Pyrex glass tube and a quartz tube coated with  $TiO_2$  film for housing a *Sparkie* FL10W/BLB mercury lamp with wavelength of 365 nm and approximately 10 W maximum output. The irradiance of the UV lamp was controlled by adjusting the variable voltage transformer, and the irradiance on the surface of quartz tube was detected by a Radiometer/Photometer (*International Light Technologies* ILT 1400) equipped with the SEL005 radiation sensor. The composition of reaction gas in the inlet stream was mixed with NO,  $NH_3$ ,  $O_2$ , and the balance gas, He. The humidity of the inlet stream was regulated by mixing the reactants-containing inlet stream with wet He of different flow rates. The temperature of inlet stream in the photoreactor was maintained at  $25^\circ C$ . The pre-warmed light source in the reactor was turned on after the temperature, flow rate, pressure, and humidity of the mixed gas were considered to be steady. The gaseous concentrations of NO, and  $NO_2$  were measured by the CLD62 NO/ $NO_x$  analyzer (*Eco Physics* CLD62). The gaseous  $N_2$  and  $N_2O$  concentrations of inlet and outlet streams were determined by a gas chromatograph (*Agilent* 7895A) equipped with a HP-PLOT 5A and a thermal conductivity detector.

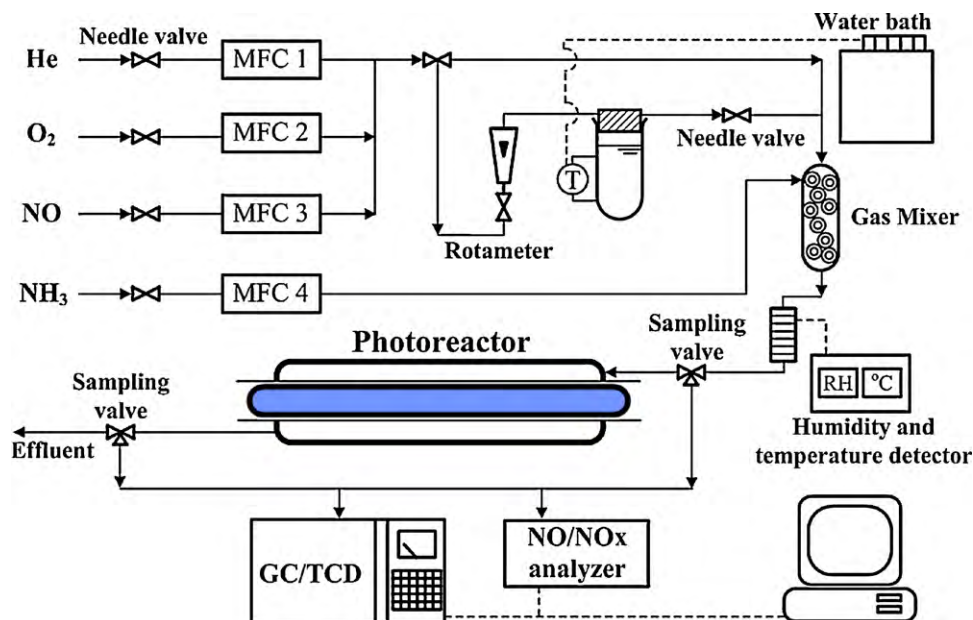


Fig. 1. Schematic diagram of the photo-SCR system.

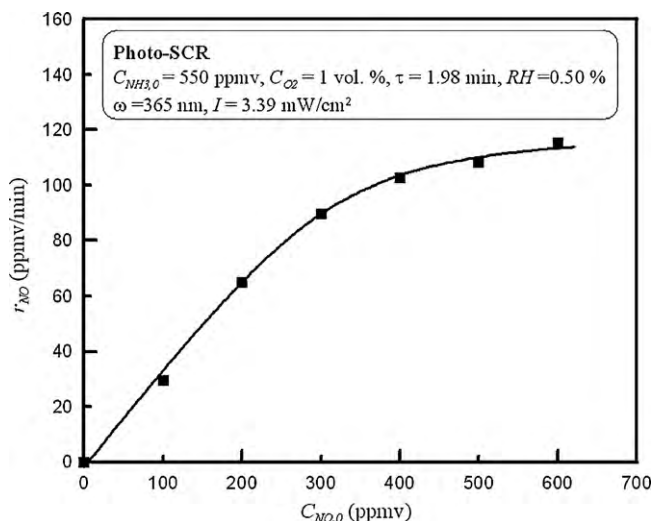


Fig. 2. Photocatalytic reduction rates of NO in the photo-SCR for experiments conducted with various inlet NO concentrations.

### 3. Results and discussion

According to the proposed mechanisms reported by previous researchers [6], the reduction of NO in the photo-SCR is the reaction between the adsorbed ammonia molecules and NO molecules in gas phase. The photocatalytic reaction rate of NO reduction by the photo-SCR with various inlet concentrations of NO in the range of 100–600 ppmv is illustrated in Fig. 2. The reduction rate of NO was significantly increased with the increase of the inlet NO concentration for experiments conducted at NO concentrations lower than 500 ppmv; therefore, the reduction of NO was limited by the NO molar flux from bulk stream onto the ammonia molecules adsorbed on the active sites of TiO<sub>2</sub>. However, reduction rate of NO tended to be less influenced by the inlet concentration of NO for experiments conducted at NO concentration higher than 500 ppmv. This phenomenon indicated that the NO molecules transfer onto TiO<sub>2</sub> surface was excessive for the adsorbed ammonia molecules and was no longer the limiting factor for the reduction of NO by photo-SCR. In order to minimize the mass transfer effect of NO, the inlet stream containing 500 ppmv NO was chosen to investigate the NO reduction by the photo-SCR for further investigation.

Fig. 3 illustrates the gaseous compositions of the outlet stream from UV-illuminated photoreactor carrying out photo-SCR with NH<sub>3</sub> under various inlet oxygen concentrations. Most of the reduced NO was converted to N<sub>2</sub>; NO<sub>2</sub> and N<sub>2</sub>O were generated only in trace amounts. N<sub>2</sub>O molecules were generated when the reduced active sites (Ti<sup>3+</sup>) reacted with NO molecules. No NO<sub>2</sub> molecules were found to be generated for NO reduction by the photo-SCR in the absence of oxygen molecules; however, NO<sub>2</sub> concentration was increased with increasing oxygen concentration due to the photocatalytic oxidation of NO molecules. The generation of NO<sub>2</sub> was found to be kept relatively constant for experiments conducted with the presence of oxygen higher than 2 vol.%. Fig. 4 shows the effect of inlet concentration of O<sub>2</sub> on the NO reduction efficiency and N<sub>2</sub> selectivity in the photo-SCR with NH<sub>3</sub> over TiO<sub>2</sub>. N<sub>2</sub> selectivity is defined as the ratio of N<sub>2</sub> concentration to the sum of N<sub>2</sub>, NO<sub>2</sub>, and N<sub>2</sub>O concentrations in the outlet stream. N<sub>2</sub> selectivity for experiments conducted with various inlet O<sub>2</sub> concentrations was found to be higher than 90%. The N<sub>2</sub> selectivity was slight decreased with the introduction of less than 2 vol.% O<sub>2</sub> because of the generation of NO<sub>2</sub> in the presence of oxygen. Reduction efficiency of NO was increased with increasing inlet concentration of O<sub>2</sub> from 0 to 1 vol.%, and then approached to a constant value for inlet O<sub>2</sub> con-

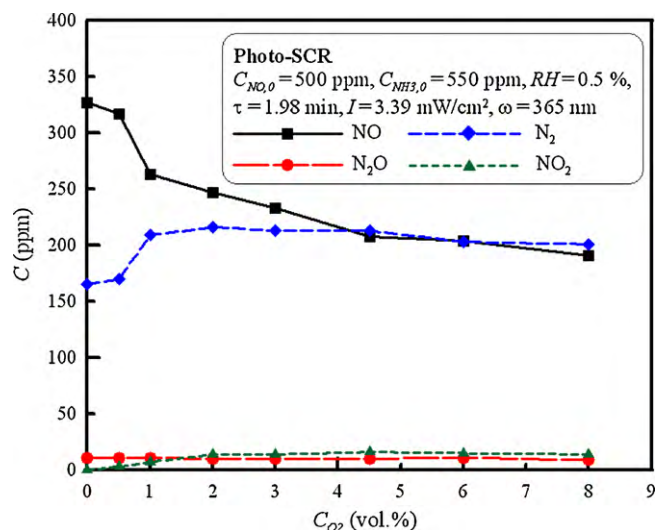


Fig. 3. Effect of inlet oxygen concentration on the gaseous composition of the outlet stream from the photoreactor.

centration higher than 1 vol.%. As the reaction mechanism of NO reduction in the photo-SCR proposed by Teramura et al. [6], O<sub>2</sub> was assumed to play important role for the re-generation of the reduced active sites of TiO<sub>2</sub> (Ti<sup>3+</sup>) during NO reduction by the photo-SCR. The re-generation reaction of Ti<sup>3+</sup> with oxygen molecules was found to be rate-determining step for cases with insufficient O<sub>2</sub>. In this study, 1 vol.% oxygen was introduced into the reaction system to sufficiently regenerate active sites of TiO<sub>2</sub> for the following study.

Table 1 illustrates the composition of the outlet stream, the NO reduction efficiency, the N<sub>2</sub> selectivity, and the apparent quantum yields ( $\phi_{NO}$ ) for NO reduction by the photo-SCR with NH<sub>3</sub> under various irradiances. The concentration of NO in the outlet stream was decreased from 290 to 225 ppmv with increasing irradiance from 2.37 to 3.73 mW/cm<sup>2</sup>, while the concentration of N<sub>2</sub> was increased from 166 to 230 ppmv. The formations of N<sub>2</sub>, NO<sub>2</sub> and N<sub>2</sub>O were found to be increased with the increase of irradiance. Experimental results shown in Table 1 also revealed that the reduction efficiency of NO was increased with the increase of UV irradiance, and almost 50% of NO reduction efficiency was achieved at the UV irradiance of 3.73 mW/cm<sup>2</sup>. The increased NO reduction efficiency was because

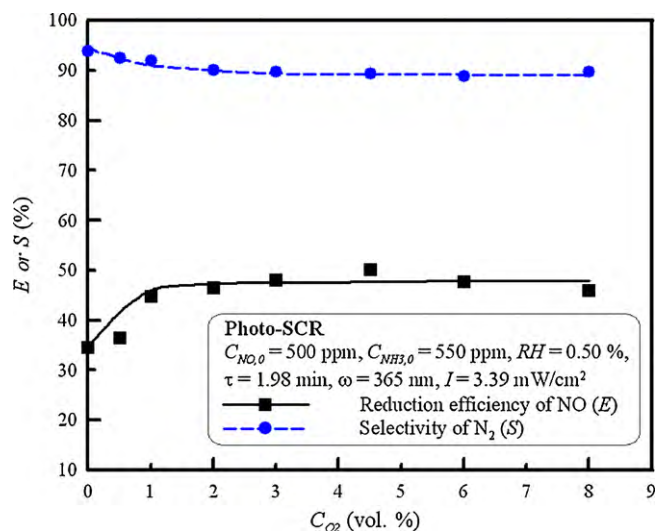


Fig. 4. Effect of inlet O<sub>2</sub> concentration on NO reduction efficiency and N<sub>2</sub> selectivity in the photo-SCR.

**Table 1**  
Effects of irradiance on the performance of NO reduction by the photo-SCR.

$I$ [mW/cm <sup>2</sup> ]	$C_{NO}$ [ppmv]	$C_{NO_2}$ [ppmv]	$C_{N_2}$ [ppmv]	$C_{N_2O}$ [ppmv]	$E$ [%]	$S$ [%]	$\phi_{NO} \times 10^2$
2.37	290	3	166	15	35	90	3.11
2.71	269	4	192	20	40	89	3.03
3.05	250	4	209	22	44	89	3.01
3.39	233	6	224	23	48	89	2.91
3.73	225	7	230	25	50	88	2.79

$C_{NO,0} = 500$  ppmv,  $C_{NH_3,0} = 550$  ppmv,  $C_{O_2} = 1$  vol.%,  $\tau = 1.98$  min,  $RH = 0.50\%$ .

that more electrons-hole pairs were generated with the increase of UV irradiance.  $N_2$  selectivity for experiments conducted at the irradiance of 2.37 mW/cm<sup>2</sup> was about 90%. The  $N_2$  selectivity was found to be slightly decreased by increasing UV irradiance. This result is ascribed to the increased concentrations of  $NO_2$  and  $N_2O$  at higher irradiance.

In this study, the apparent quantum yields were calculated with incident photons of UV light, assuming all incident photons encountered the photocatalyst as absorbed photons and neglecting the occurrence of reflection, scattering, transmission and absorption of photons [14]. The apparent quantum yields for NO reduction ( $\phi_{NO}$ ) were defined as the ratio of the reaction rate to the photons absorption rate, that is,

$$\phi_{NO} = \frac{\text{moles of NO reduction}}{\text{moles of photons absorbed}} \approx \frac{\Delta C_{NO} \cdot V}{I_{\text{abs}}/U \cdot \tau} \quad (1)$$

where the  $U$  is the energy per mole photons at the wavelength of 365 nm ( $U = 3.28 \times 10^5$  J/mol);  $V$  and  $\tau$  are the effective volume (cm<sup>3</sup>) and the retention time (min) of photoreactor. As the experimental results shown in Table 1, the apparent quantum yields for NO reduction were found to be decreased with the increase of UV irradiance possibly ascribed to the limited surface area of  $TiO_2$  to absorb excessive light energy.

The composition of out stream, the NO reduction efficiency, the  $N_2$  selectivity, and the apparent quantum yields ( $\phi_{NO}$ ) for NO reduction by the photo-SCR with various inlet ammonia concentrations are shown in Table 2. Generation of  $NO_2$  was found to be less influenced by the inlet concentration of  $NH_3$  because  $NO_2$  was generated mainly by the photocatalytic oxidation of NO.  $N_2O$  concentrations were increased with increasing inlet  $NH_3$  concentration because more reduced active sites ( $Ti^{3+}$ ) were generated at higher  $NH_3$  concentration. Experimental results shown in Table 2 also indicated that both the NO reduction efficiency and the apparent quantum yields for NO reduction were increased with the increase of  $NH_3$  concentration because more  $NH_2$  radicals generated photocatalytically from adsorbed  $NH_3$  molecules. Approximately 90% of  $N_2$  selectivity was also observed in the photo-SCR with various inlet  $NH_3$  concentrations.

The influence of water content of inlet stream on the NO reduction by the photo-SCR is presented in Table 3. The relative humidity of inlet stream, used in this experiment, was in the range of 0.5–50%. The NO reduction efficiency and the apparent quantum yields for NO reduction decreased rapidly with the relative humidity, while only 6% of NO molecules were photocatalytically reduced by photo-SCR with the relative humidity of 50%. The selectivity of  $N_2$  was also found to be decreased from 89% to 54% with increasing relative humidity from 0.5% to 50%. The decreased NO reduction efficiency with increasing water content is contributed to the competitive adsorption of water and  $NH_3$  molecules for the active sites on  $TiO_2$  by previous researchers [9].

As the composition data of the outlet stream shown in Table 3, the concentration of  $NO_2$  was found to be increased with increasing relative humidity of inlet stream because water molecules might improve the photocatalytic oxidation of NO molecules. From the experimental results, it is concluded that water molecules play a

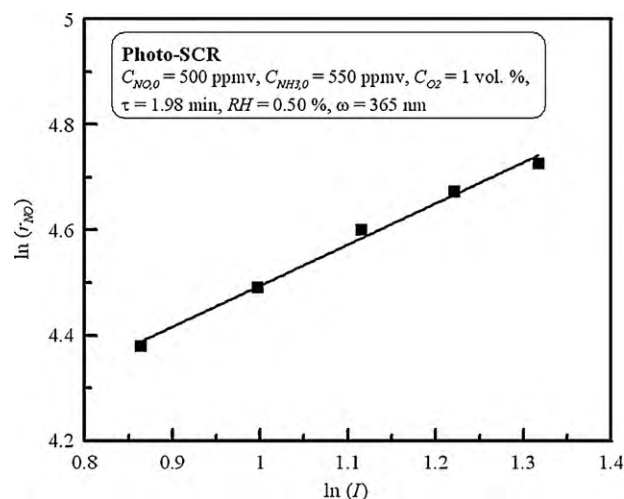
vital role in the reduction reaction of NO by photo-SCR. The increase of water content in the inlet stream promoted the photocatalytic oxidation of NO to generate  $NO_2$  molecules, while the generation of  $N_2O$  molecules was restricted due to the favorable adsorption of water molecules for the reduced active sites ( $Ti^{3+}$ ). In addition, water molecules may compete with  $NH_3$  molecules on the active site ( $Ti^{4+}$ ) of  $TiO_2$ . The competitive adsorption of water and  $NH_3$  molecules on the active sites of  $TiO_2$  caused the decrease of NO reduction efficiency.

According to previous studies [10,11], the dependence of photocatalytic NO reduction rate on irradiance could be expressed by a power function. Taking the natural logarithm of both sides of the power function, the reaction order against UV irradiance,  $n$ , for photo-SCR reaction can be obtained from the plotted curve using  $\ln(r_{NO})$  versus  $\ln(I)$ . The kinetic regression results are shown in Fig. 5, that is,

$$\ln(r_{NO}) = 0.78 \ln(I) + 3.71 \quad (2)$$

The reaction order of UV irradiance against the reduction rate of NO by photo-SCR was found to be 0.78. The reaction order against UV irradiance lower than unity for photo-SCR is possibly because that the promotion of electron-hole pairs recombination can be found for experiments conducted at excessive UV irradiance [12], therefore decreasing the dependence of NO conversion on the irradiance. Several previous studies indicated that the reaction order with respect to the UV irradiance was ranging between 0.5 and 1.0 for most photocatalytic reactions [11,12].

Based on the proposed mechanisms reported by previous researchers as presented in the Introduction Section, the reduction mechanism of NO in the photo-SCR was assumed to be described by Eley–Rideal model, and the rate-determining step was determined as the decomposition of  $NH_2NO$ .  $NH_3$  molecules are assumed to be adsorbed on the active sites, and then react with NO molecules to carry further reaction. Experimental results implied that water



**Fig. 5.** Kinetic regressions for the photoassisted selective catalytic reduction of NO under various irradiances.

**Table 2**  
Effects of initial ammonia concentration on the performance of NO reduction by the photo-SCR.

$C_{\text{NH}_3,0}$ [ppmv]	$C_{\text{NO}}$ [ppmv]	$C_{\text{NO}_2}$ [ppmv]	$C_{\text{N}_2}$ [ppmv]	$C_{\text{N}_2\text{O}}$ [ppmv]	$E$ [%]	$S$ [%]	$\phi_{\text{NO}} \times 10^2$
100	331	7	128	12	27	87	1.69
200	280	8	175	14	38	89	2.32
300	263	9	189	16	41	88	2.54
400	251	9	199	18	44	88	2.68
500	240	8	206	19	46	89	2.79
550	231	6	224	23	48	89	2.89
600	232	8	213	21	47	88	2.86

$C_{\text{NO},0} = 500$  ppmv,  $C_{\text{O}_2} = 1$  vol.%,  $I = 3.39$  mW/cm<sup>2</sup>,  $\tau = 1.98$  min,  $\text{RH} = 0.50\%$ .

**Table 3**  
Effects of inlet relative humidity on the performance of NO reduction by the photo-SCR.

Relative humidity [%]	$C_{\text{NO}}$ [ppmv]	$C_{\text{NO}_2}$ [ppmv]	$C_{\text{N}_2}$ [ppmv]	$C_{\text{N}_2\text{O}}$ [ppmv]	$E$ [%]	$S$ [%]	$\phi_{\text{NO}} \times 10^2$
0.5	238	6	224	23	48	89	2.97
1	258	10	216	20	43	88	2.70
5	309	13	146	18	32	82	2.01
10	339	13	116	17	25	79	1.59
15	361	14	94	16	20	76	1.27
20	380	14	82	16	17	73	1.03
25	406	16	64	14	11	68	0.70
30	417	18	61	13	8	66	0.51
40	427	18	43	12	7	59	0.39
50	426	21	40	13	6	54	0.40

$C_{\text{NO},0} = 500$  ppmv,  $C_{\text{NH}_3,0} = 550$  ppmv,  $C_{\text{O}_2} = 1$  vol.%,  $I = 3.39$  mW/cm<sup>2</sup>,  $\tau = 1.98$  min.

molecules may compete with NH<sub>3</sub> molecules for same active sites to inhibit the reduction efficiency of NO. Illuminated UV light was emitted from a hypothetical line source located at the center of the reactor in this study. The reflection or refraction of light at all interfaces was assumed to be negligible [13,14]. Combining the effect of UV irradiance, the reduction rate of NO in the photo-SCR with ammonia in the presence of oxygen over TiO<sub>2</sub> can be expressed as follow:

$$r_{\text{NO}} = k_a I^{0.78} \frac{C_{\text{NO}} C_{\text{NH}_3}}{1 + K C_{\text{NH}_3} + K K_s C_{\text{NO}} C_{\text{NH}_3} + K^* C_{\text{H}_2\text{O}}} \quad (3)$$

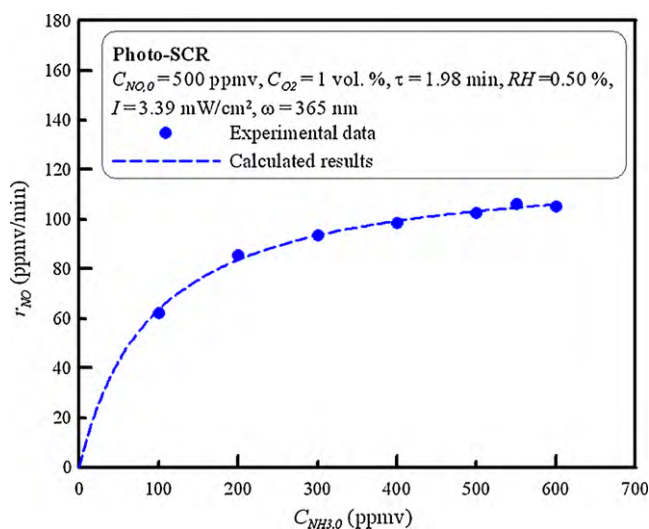
where  $r_{\text{NO}}$  is the reduction rate of NO in the photo-SCR (ppmv/min);  $C_{\text{NO}}$ ,  $C_{\text{NH}_3}$ , and  $C_{\text{H}_2\text{O}}$  are the concentrations (in ppmv) of NO, NH<sub>3</sub> and water molecule, respectively; and  $I$  is the irradiance of UV lamp (mW/cm<sup>2</sup>). In addition,  $k_a$ ,  $K_s$ ,  $K$  and  $K^*$  are the apparent reaction rate constant, the surface reaction equilibrium constant and the adsorption constants of ammonia and water molecule, respectively.

The rate law parameters,  $k_a$ ,  $K_s$ ,  $K$  and  $K^*$ , are determined and listed in Table 4 by regressing experimental data for reduction of NO by photo-SCR conducted with the irradiance of 3.39 mW/cm<sup>2</sup> under various concentrations of NO, NH<sub>3</sub> and H<sub>2</sub>O. By inserting these coefficients into Eq. (3), the reduction rate of NO in the photo-SCR under various operating conditions can be correlated by the Eley–Rideal type kinetic model.

As the results shown in Figs. 6 and 7, fairly good agreements were found between the experimental results and the calculated values for the reduction rate of NO in the photo-SCR conducted under various NH<sub>3</sub> concentrations and relative humidities. These facts infer that the kinetic equation proposed in this study is applicable for NO reduction by the photo-SCR in the presence of oxygen. As the results shown in Fig. 6, reduction rate of NO increased rapidly with NH<sub>3</sub> concentration because more ammonia molecules were adsorbed on active sites of TiO<sub>2</sub>. Almost no enhancement of NO reduction rate was observed for experiments conducted with NH<sub>3</sub> concentration higher than 400 ppmv because of the limited active sites on the surface of TiO<sub>2</sub>. Teramura et al. [7] investigated the kinetic study of the photo-SCR and depicted that the NH<sub>3</sub> concentration ranged from 500 to 1250 ppmv was independent of the NO conversion in the photo-SCR. Fig. 7 reveals that the NO reduction rate was found to be decreased with increasing relative humidity

due to the competitive adsorption of water and NH<sub>3</sub> molecules on the active sites of TiO<sub>2</sub>.

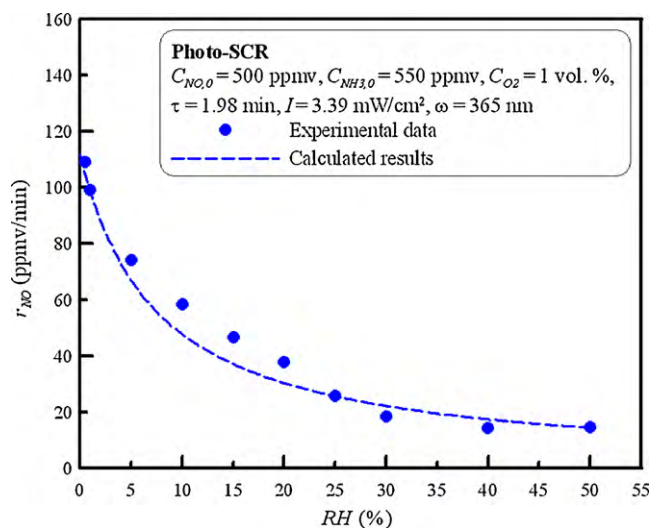
The calculated results of NO reduction by the photo-SCR operated at various retention times agreed fairly well with the available experimental data as depicted in Fig. 8. Reduction efficiency of NO was elevated with the increase of retention time. Greater than 70% of NO reduction efficiency can be achieved for experiments conducted at room temperature at retention time more than 4 min. For current applications, SCR using V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst could attain NO reduction efficiency of 70–90% at operating temperatures higher than 300 °C at retention time less than 1 s [15]. Even though the application of photo-SCR can be processed at room temperature, the retention times required are much longer than those for SCR to achieve satisfactory NO reduction efficiency. Therefore, the modification of photocatalyst to effectively utilize the incident photons under practical operational conditions is vital for applications of photo-SCR in the real processes.



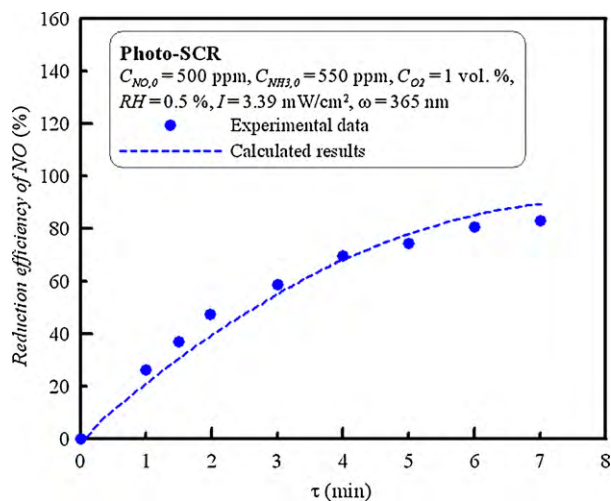
**Fig. 6.** Calculated and experimental results of NO reduction rate for NO reduction by photo-SCR with various inlet ammonia concentrations.

**Table 4**  
Reaction coefficients in Eq. (3) for the photo-SCR of NO.

$n$	$k_a$ [(mW/cm <sup>2</sup> ) <sup>-0.78</sup> ppmv <sup>-1</sup> min <sup>-1</sup> ]	$K$ [ppmv <sup>-1</sup> ]	$K_s$ [ppmv <sup>-1</sup> ]	$K^*$ [ppmv <sup>-1</sup> ]
0.78	$1.8 \times 10^{-3}$	$6.2 \times 10^{-3}$	$4.2 \times 10^{-3}$	$5.2 \times 10^{-3}$



**Fig. 7.** Calculated and experimental results of NO reduction rate for NO reduction by photo-SCR with various inlet relative humidities.



**Fig. 8.** Calculated and experimental results of NO reduction by photo-SCR at various retention times.

#### 4. Conclusions

The performance of NO reduction by the photo-SCR under various irradiances, inlet concentrations of O<sub>2</sub>, NO, NH<sub>3</sub> and H<sub>2</sub>O, and retention time of inlet stream at room temperature was presented. Reduction rate of NO was less influenced by the inlet concentration of NO for experiments conducted with NO concentration higher than 500 ppmv. In this study, introduction of 1 vol.% oxygen into the reaction system was sufficiently to regenerate the active sites on TiO<sub>2</sub>. More than 70% of NO was reduced by photo-

SCR with the retention time more than 4 min. Most NO molecules consumed were photocatalytically reduced to form N<sub>2</sub>; however, N<sub>2</sub>O molecules were generated when certain NO molecules were reduced by the reduced active sites (Ti<sup>3+</sup>) in the presence of oxygen. N<sub>2</sub> selectivity and NO reduction efficiency were decreased with the introduction of water molecules in the inlet stream mainly because of the competitive adsorption of water and NH<sub>3</sub> molecules for the active sites on TiO<sub>2</sub> surface. Reduction of NO was found to be increased with the increase of UV irradiance and NH<sub>3</sub> concentration. The reaction order against UV irradiance was lower than unity for the photo-SCR of NO because excessive irradiance possibly promoted the recombination of electron-hole pairs. For experiments conducted with NH<sub>3</sub> concentration higher than 400 ppmv, NO reduction rate approached to a constant value because of the limited active sites on the surface of TiO<sub>2</sub>. The reaction behavior of the NO reduction by the photo-SCR was satisfactorily illustrated by Eley–Rideal kinetics.

#### Acknowledgements

This research was supported by Grant NSC-96-2628-E-011-001-MY3 from the National Science Council, Taiwan, Republic of China.

#### References

- [1] H. Bosch, F. Janssen, Formation and control of nitrogen oxides, *Catal. Today* 2 (1988) 369–531.
- [2] S.M. Cho, Properly apply selective catalytic reduction for NO<sub>x</sub> removal, *Chem. Eng. Prog.* 90 (1994) 39–45.
- [3] B. Huang, R. Huang, D. Jin, D. Ye, Low temperature SCR of NO with NH<sub>3</sub> over carbon nanotubes supported vanadium oxides, *Catal. Today* 126 (2007) 279–283.
- [4] R. Jin, Z. Wu, Y. Liu, B. Jiang, H. Wang, Photocatalytic reduction of NO with NH<sub>3</sub> using Si-doped TiO<sub>2</sub> prepared by hydrothermal method, *J. Hazard. Mater.* 161 (2009) 42–48.
- [5] T. Tanaka, K. Teramura, K. Arakaki, T. Funabiki, Photoassisted NO reduction with NH<sub>3</sub> over TiO<sub>2</sub> photocatalyst, *Chem. Commun.* (2002) 2242–2743.
- [6] K. Teramura, T. Tanaka, T. Funabiki, Photoassisted selective catalytic reduction of NO with ammonia in the presence of oxygen over TiO<sub>2</sub>, *Langmuir* 19 (2003) 1209–1214.
- [7] K. Teramura, T. Tanaka, S. Yamazoe, K. Arakaki, T. Funabiki, Kinetic study of photo-SCR with NH<sub>3</sub> over TiO<sub>2</sub>, *Appl. Catal. B* 53 (2004) 29–36.
- [8] S. Yamazoe, T. Okumura, K. Teramura, T. Tanaka, Development of the efficient TiO<sub>2</sub> photocatalyst in photoassisted selective catalytic reduction of NO with NH<sub>3</sub>, *Catal. Today* 111 (2006) 266–270.
- [9] E. Garcia-Bordeje, J.L. Pinilla, M.J. Lazaro, R. Moliner, NH<sub>3</sub>-SCR of NO at low temperatures over sulphated vanadia on carbon-coated monoliths: effect of H<sub>2</sub>O and SO<sub>2</sub> traces in the gas feed, *Appl. Catal. B* 66 (2006) 281–287.
- [10] M. Mohseni, A. David, Gas phase vinyl chloride (VC) oxidation using TiO<sub>2</sub>-based photocatalysis, *Appl. Catal. B* 46 (2003) 219–228.
- [11] C.M. Ma, Y. Ku, Y.L. Kuo, Y.C. Chou, F.T. Jeng, Effects of silver on the photocatalytic degradation of gaseous isopropanol, *Water Air Soil Pollut.* 197 (2009) 313–321.
- [12] S.B. Kim, S.C. Hong, Kinetic study for photocatalytic degradation of volatile organic compounds in air using thin film TiO<sub>2</sub> photocatalyst, *Appl. Catal. B* 35 (2002) 305–315.
- [13] Y. Ku, C.M. Ma, Y.S. Shen, Decomposition of gaseous trichloroethylene in a photoreactor with TiO<sub>2</sub>-coated nonwoven fiber textile, *Appl. Catal. B* 34 (2001) 181–190.
- [14] C.M. Ma, Y. Ku, Y.C. Chou, F.T. Jeng, Performance of tubular-type optical fiber reactor for decomposition of VOCs in gaseous phase, *J. Environ. Eng. Manage.* 18 (2008) 363–369.
- [15] T. Curtin, Selective catalytic reduction of NO<sub>x</sub>, in: V.H. Grassian (Ed.), *Environmental Catalysis*, CRC Press, Boca Raton, 2005, pp. 197–210.