

## Removal of Indoor Air ppb Level Volatile Organic Compounds (VOCs) and NO<sub>x</sub> by Heterogeneous Photocatalysis

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### ABSTRACT

VOCs and NO<sub>x</sub> are the major pollutants in Hong Kong indoor environment. Traditional air purification method such as adsorption by activated carbon is not reliable and get saturated easily. Adsorption merely transfers pollutants from gaseous phase to solid phase and poses the disposal problem. Using photocatalysis, however, strong oxidant such as hydroxyl radical is generated and actually oxidized the pollutant to H<sub>2</sub>O and CO<sub>2</sub>. In this study, semi-conductor TiO<sub>2</sub> is used with 365 nm ultra violet light as activation energy. 35 ppb of benzene, toluene, ethylbenzene and o-xylene (BTEX) were used as target VOCs and 200 ppb NO was used. Sensitive analyses of the photodegradation of NO<sub>x</sub> and BTEX are conducted by investigating the effect of residence time and relative humidity. NO, NO<sub>2</sub>, and NO<sub>x</sub> are simultaneously measured by a Chemiluminescence NO analyzer. BTEX were collected by Summa canister and analyzed by GC/MS. It was found that a minimum of 60% and a maximum of 85% of NO<sub>x</sub> are removed from the system under different variations. Removal efficiencies of NO<sub>x</sub> are higher at a longer resident time and at a lower relative humidity higher and light intensity. Relative humidity affected the photoefficiency most significantly. The presence of NO promoted the photodegradation of BTEX. The presence of BTEX, however, inhibited the photodegradation of NO.

### 1.0 INTRODUCTION

People generally spend more than 80% of their time in indoor environment [1]. The quality of indoor air has a direct impact on human health in terms of lengthened exposure to pollutants by inhalation. NO and VOCs were chosen as target pollutants for this study. NO is one of the major pollutants in indoor environments. Among numerous compounds which belong to VOCs, benzene, toluene, ethylbenzene and o-xylene (BTEX) are chosen for this study. The reason is that BTEX is the major VOCs found in indoor environments in different countries [2,3]. In Hong Kong, BTEX are also the major VOCs found in an indoor environment, either in mechanically ventilated buildings or in residential homes. The concentration of BTEX usually found in this environment ranged from 10 ppb to 100 ppb [4,5]. There is a limited study on the photodegradation of pollutants at typical indoor levels. Photodegradation of toluene and benzene at several hundreds ppb levels was conducted with a conversion of around 80% and 95% respectively. However, the concentration used was several hundreds ppb, which is seldom found in normal and polluted indoor environment such as offices and residential homes.

In this study, we investigated the photodegradation of BTEX and NO at parts per billion levels with reference to the typical indoor air pollutant concentrations in Hong Kong. As reported in previous study [6], the photodegradation rate increased with increasing concentrations of the pollutants in the range of several hundreds ppm level. It is vital to investigate if the photodegradation rate will reduce immensely at indoor ppb levels. The effects of residence time and levels of humidity on the photodegradation rate were also conducted. As NO and BTEX usually co-exist in indoor environments, the effects of concurrent photodegradation of NO and BTEX is also investigated to evaluate the feasibility of photocatalytic technology for indoor air purification.

### 2.0 EXPERIMENTAL

BTEX (Spectra gases) and NO (BOC gases) were generated from standard gas. TiO<sub>2</sub> (Degussa P-25) was used as a photocatalyst. The weight of TiO<sub>2</sub> imposed is determined by the weight difference before and after the coating procedure. In all experiments, the weight of TiO<sub>2</sub> imposed is 1.64 g ± 5%. A reactor with a volume of 57 liter (40.5H x 50.5L x 28W cm) with its surface coated by a Telfon film (BYTAC Type AF-21) was used for this study. Illumination was provided by a 6W UV lamp (Cole-Parmler) which emits a primary wavelength at 365 nm and its intensity was determined by a UV meter (Spectroline DRC-100X). Other experimental details are reported in elsewhere [7].

### 3.0 RESULT and DISCUSSION

A typical experiment of photocatalytic oxidation of NO at room temperature with an initial concentration of 200 ppb, residence time 11.4 minutes and 10% relative humidity is shown in Fig. 1. When the UV light is switched on, the NO concentration dropped rapidly and reached a photo-steady-state in 5 minutes with a conversion of 94%. NO concentration rose immediately when the lamp switched off. Upon reaching at 200 ppb, the UV light turned on again and reached its photo-steady state concentration. Prior to this experiment, a dark test is performed. Under the same experimental conditions with the absent of UV light, using TiO<sub>2</sub> solely could not reduce NO concentration.

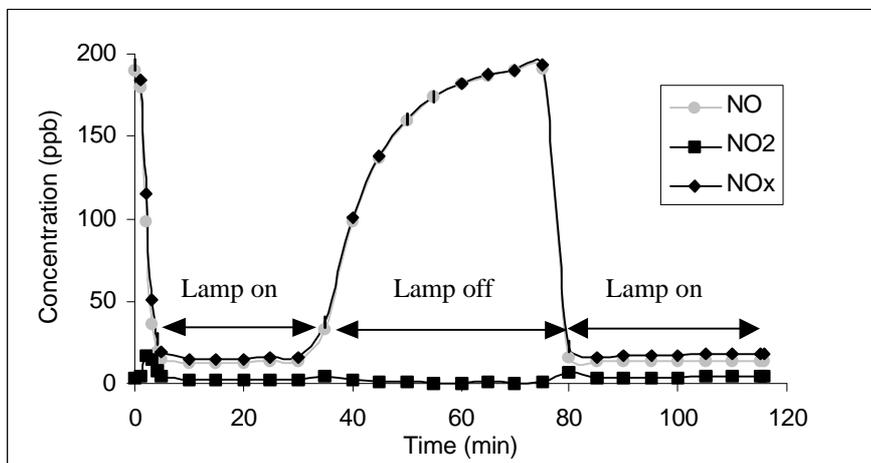


Figure 1. Photodegradation of NO at 200 ppb.

According to equation 1, the conversion of NO generates NO<sub>2</sub>. However, in our study the generation of NO<sub>2</sub> during photodegradation of NO is less related to residence time. At a residence time of 11.40 min, the concentration of NO<sub>2</sub> is remarkably lower, as shown in Fig. 2. For residence time between 2.85 min to 3.80 min, the concentrations of NO<sub>2</sub> are similar. On the one hand, at a shorter residence time with lower NO conversion, less NO<sub>2</sub> was generated from NO. On the other hand, at a longer residence time, the generated NO<sub>2</sub> have more contact time to be adsorbed on the filter forming HNO<sub>3</sub>, which decreased the amount of NO<sub>2</sub> exiting to the outlet stream. These two phenomena under different residence time provided a relatively stable NO<sub>2</sub> concentration in the outlet stream.

The impact on the photodegradation of NO under different levels of relative humidity was evaluated in Fig. 3. The conversion of NO decreased with increasing relative humidity. The conversion of NO decreased from 81% to 60% when the relative humidity increased from 10% to 75%. The generation of NO<sub>2</sub> followed a similar trend. At a higher relative humidity (75%), 45 ppb of NO<sub>2</sub> is generated and at lower relative humidity (10%), only 8.4 ppb of NO<sub>2</sub> is generated. Presumably, at higher relative humidity, more hydrogen ions (H<sup>+</sup>) and hydroxide ions (OH<sup>-</sup>) are dissociated from water vapor. The hydrogen ions (H<sup>+</sup>) react with superoxide (O<sub>2</sub><sup>-</sup>) forming HO<sub>2</sub><sup>·</sup>. According to Equation 1, more HO<sub>2</sub><sup>·</sup> react with NO forming more NO<sub>2</sub> at a higher relative humidity. Although at a higher relative humidity more NO reacts with HO<sub>2</sub><sup>·</sup>, the concentration of NO exited the outlet stream is still higher with

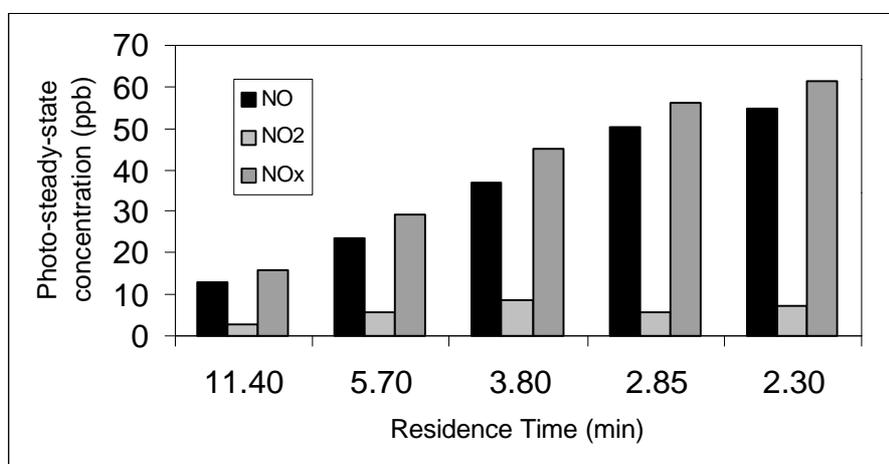


Figure 2 Variation of photo-steady-state concentration at different residence time.

increasing relative humidity. This is probably due to the fact that equation 2 took place, which generated 2 molecules of NO with one molecule of NO and NO<sub>2</sub>, with the assistance of higher water content. Murata and others [8] also reported the photodegradation of NO decreased with increasing relative humidity at a concentration of 1 ppm. Using ppb level as inlet pollutant concentration, the effect of water content is more predominant. The ratio of water content to pollutant level is the highest in our study.

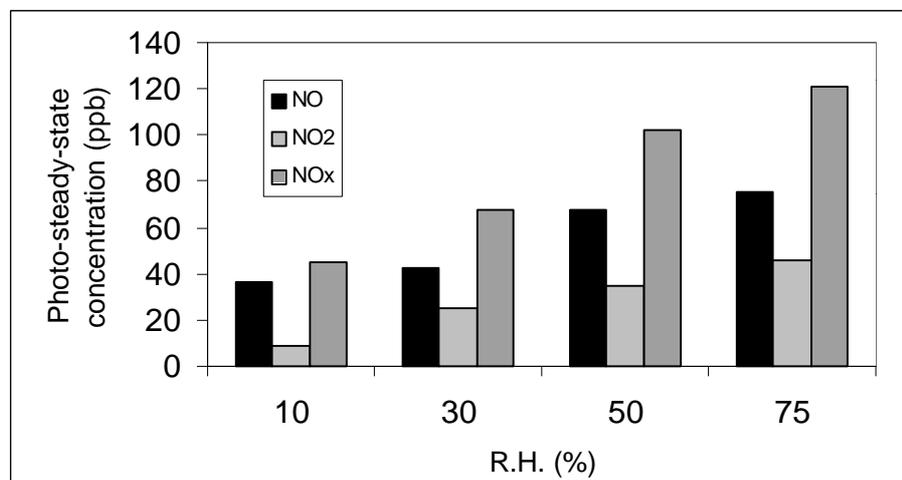
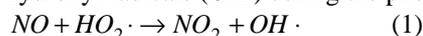


Figure 3 Variation of photo-steady-state concentration at different relative humidity.

Variations of residence time were tested to evaluate the photodegradation activity of BTEX and NO. Fig. 4 shows the photodegradation of 35 ppb BTEX with the presence of 200 ppb NO at a humidity level of 2100 ppmv. Results showed that the conversion decreased with decreasing residence time. It can be assumed that a longer residence time, a higher rate of contact and length of contact time were achieved between the pollutants and the hydroxyl radicals, resulting in a higher conversion.

As shown in figure 4, the conversion of BTEX with the presence of NO is higher than BTEX solely under different residence time. The enhancement of BTEX conversion is due to the generation of hydroxyl radicals (OH·) during the photodegradation of NO, as shown in equation 1 and 2 [9].



Or the NO<sub>2</sub> generated reacts with NO form 2 hydroxyl radicals and 2 NO molecules as follows:



The addition of NO resulted the highest enhancement effect for benzene and toluene. This is probably due to the reaction rate of OH radicals of ethylbenzene and o-xylene being comparatively higher than benzene and toluene [10]. The enhancement effect of NO may be hindered by the high conversion of ethylbenzene and o-xylene. Also noted is, the decrease in enhancement effect paralleled the decreasing residence time. At a shorter residence time, BTEX have a lower colliding frequency with the hydroxyl radicals generated from the photodegradation of NO. The enhancement effect is reduced with decreasing residence time.

Fig. 4(b) shows the photodegradation of NO with the presence and absence of BTEX. With the presence of BTEX, the NO conversion is lower and generated a lower secondary pollutant NO<sub>2</sub>. The overall NO<sub>x</sub> conversion is also lower with the presence of BTEX under different residence times. The lower NO<sub>2</sub> generation can be explained by the lower conversion of NO, as shown in equation 1. Similar to the photodegradation of BTEX, NO conversion, with or without BTEX, decreased with decreasing residence time.

#### 4.0 CONCLUSION

Removal of NO using photocatalytic technology is feasible for improving indoor air quality. Using TiO<sub>2</sub> as photocatalyst, it has a high conversion of NO of over 90% in our study. Conversion of NO will generate an unfavorable secondary pollutant NO<sub>2</sub>. The efficiency of the photodegradation is vitally and adversely affected by the increasing in relative humidity. The promotion effect of NO was achieved by the OH radicals generated from the photodegradation. As NO is not the only pollutant exists in indoor environment, more research should be preformed to evaluate the effects of multi-pollutants photodegradation.

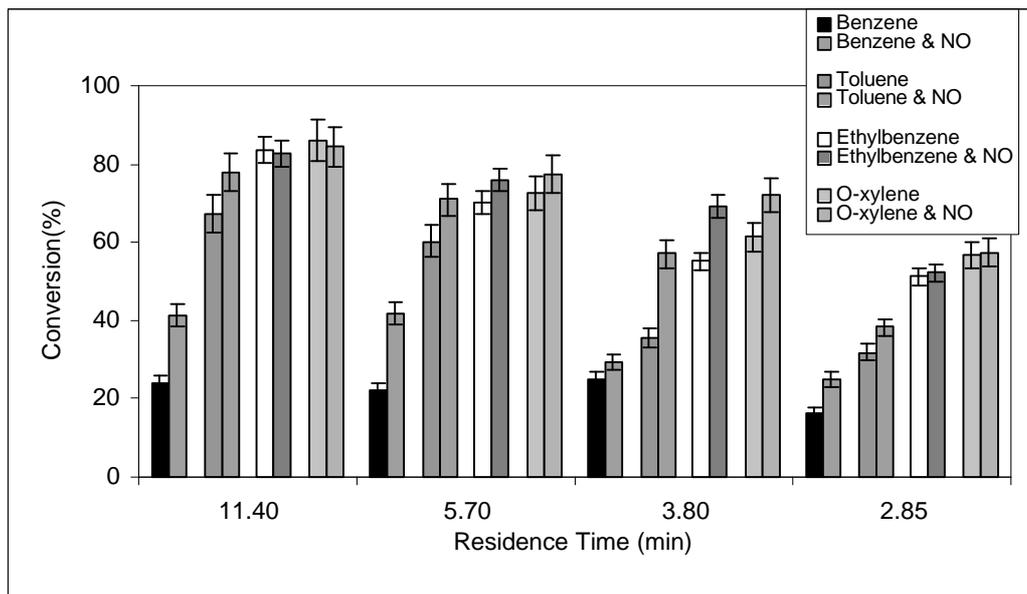


Figure 4 Variation of BTEX with/without at different residence time.

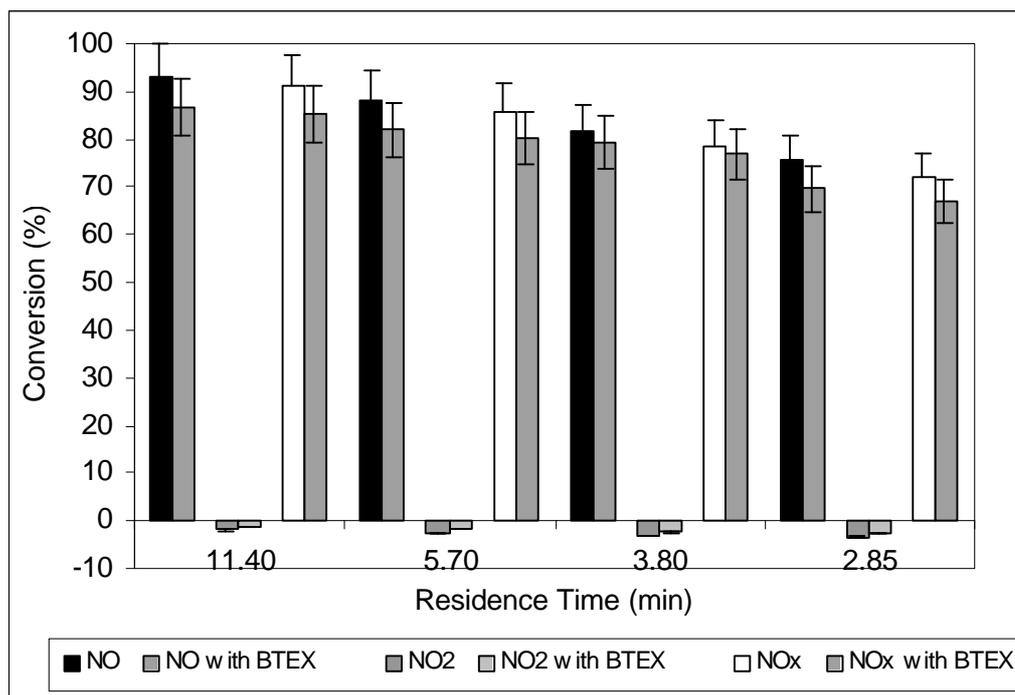


Figure 5 Variation of NO with/without BTEX at different residence time.

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