Experimental Study and Modeling of the Photocatalytic Oxidation of No in Indoor Conditions

Q.L. Yu, H.J.H. Brouwers, and M.M. Ballari

Abstract. Heterogeneous photocatalytic oxidation (PCO) has shown to be a promising air purifying technology. Nitrogen monoxide (NO) is one common indoor air pollutant. The present paper addresses the PCO reaction in indoor conditions using NO as target pollutant with the gypsum plasterboard as a special substrate and carbon-doped TiO_2 as photocatalyst. A photocatalytic reaction setup is introduced for the assessment of the indoor air quality. The PCO effect of the carbon-doped TiO_2 is evaluated using different light wavelengths. Furthermore, the influence of the reactor volume on the PCO rate is studied. The Langmuir-Hinshelwood model is applied to describe the photocatalytic reaction mechanism. Experimental results show the validity of the L-H model in the present research. Using this model, a mathematical expression is proposed to describe the concentration change in the reactor.

1 Introduction

To indoor air quality (IAQ) has been paid much attention because of the important role it plays on human beings. NO_x (NO and NO_2) and Volatile Organic Compounds (VOCs) in indoor air can be emitted from building materials, furniture, heating sources, cooking, tobacco smoke, and the pollutant can even come from outside. Photocatalytic oxidation (PCO) has been studied since 1970s [2, 6, 7] and shown as an effective technology for outdoor air pollution control in building materials [8, 9].

The present research addresses indoor air quality using the photocatalytic technology. Gypsum plasterboard is used as substrate material for the application

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of photocatalyst in this research, because it is used widely as an indoor wall board owing to its good fire resistance and aesthetics properties. A PCO setup for indoor air purifying research was developed. NO is chosen as the target pollutant in the first research stage.

2 Experimental

TiO_2 is widely used as photocatalyst because of its excellent properties like safety, low price, stability, and high photocatalytic efficiency [11]. However, TiO_2 can only be activated by UV light which is only 0.1-5 $\mu W/m^2$ in indoor illumination [10]. A modified photocatalyst is used in this research to utilize the visible light, which is carbon-doped TiO_2 (Kronos, Germany) with a cut-off wavelength of 535 nm (band gap of 2.32eV) that corresponds to bluish green light [3]. The carbon-doped TiO_2 was deposited onto the glass fibres, which were then sprayed onto the gypsum plasterboard paper with a good bonding between them.

The schematic diagram of the PCO setup for indoor air assessment is shown in Fig. 1. The setup, made from non-adsorbing plastic materials with a size of 100 × 200 mm^2 (W × L), is developed according to standard ISO 22197-1 [1]. The experimental setup is composed of the reactor, visible light source, gas supply, analyzer, parameters controller. A detailed description can be found in [9]. The applied visible light source is composed of three cool day light lamps of each 25 W (Philips, The Netherlands), emitting a visible radiation in the range of 400 to 700 nm. The light intensity can be adjusted with a light intensity controller, is measured using a VIS-BG radiometer (Dr. Gröbel UV-Elektronik GmbH, Germany).

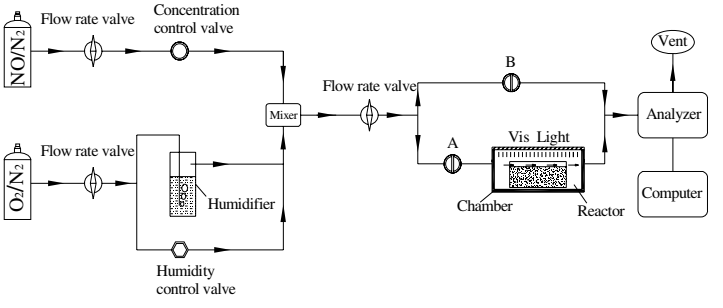

Fig. 1 Schematic diagram of photocatalytic oxidation setup

3 Results

PCO can be divided into three main steps: (1) mass transport and adsorption of pollutants from the bulk air to the surface of catalyst; (2) PCO on the catalyst; (3) desorption and mass transport of the reaction products from the surface of catalyst to air. The theory behind the PCO of NO can be found [4, 5, 12].

Recovery test of the samples was carried out by letting NO flows through the reactor in the dark. Results indicate that no photocatalytic reaction takes place in the dark and the average recovery efficiency is 97.6% shown as Table 1.

The photocatalytic reaction takes place immediately when the sample is exposed to the visible light. A total reaction time of 30 minutes was employed in the present research. The conversion of NO is calculated using equation (1).

$$Degradation(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \tag{1}$$

where C_{in} is the initial NO concentration and the C_{out} is the average pollutant concentration at exit during the last 5 minutes in the measurement time. According to PCO reactions, the NO_2 produced during the PCO could not turn into NO_3^- completely, so the exit pollutant concentration is calculated as the total of exit NO and NO_2 concentrations. Table 1 shows some PCO results.

Table 1 PCO of NO. Experimental conditions: flow rate: 3 L/min; light intensity: 10 W/m^2; relative humidity: 50 %; room temperature (21.1-22.9 °C). Concentration unit: ppm

C_{in}	C_{NO} at 10 min	Exit C_{NO}	Exit C_{NO2}	Recovery (%)	Degradation (%)
0.0992	0.0963	0.0280	0.0107	96.3	61.30
0.3003	0.2929	0.1519	0.0306	97.6	39.17
0.5002	0.4928	0.3158	0.0401	98.6	28.82
1.0010	0.9767	0.7785	0.0524	97.7	16.91

4 Kinetic Studies

The Langmuir-Hinshelwood (L-H) rate model has been employed to describe the reaction in gas-solid phase for heterogeneous photocatalysis [8]:

$$r = \frac{kKC}{1 + KC} \tag{2}$$

where r is the oxidation rate (mg/m^{2}s), k is the rate constant (mg/m^{2}s), K is the adsorption constant (m^3/mg), and C is the initial NO concentration (mg/m^3).

Along the longitudinal of the reactor, the NO mass balance reads:

$$r_{NO} = v_{air} \frac{dC}{dx} = -a_v r = -a_v \frac{kKC}{1 + KC} \tag{3}$$

where v_{air} (m/s) is the linear air flow rate along the reactor, and a_v (1/m), with a_v=A/V, as the active surface area per reactor volume because the PCO reaction only occurs in the sample surface, A (m^2) is the active surface area of the sample (in the present study, A=LW) and V (m^3) is the reactor volume (V=LWH), L, W, and H are the length, the width, and the height of the reactor, respectively.

Expression (4) is obtained by solving differential equation (3) considering the boundary condition C(x = 0) = C_{in}, yielding:

$$\frac{WL}{Q(C_{in}-C_{out})}=\frac{1}{k}+\frac{1}{kK}\frac{Ln(C_{in}/C_{out})}{(C_{in}-C_{out})} \tag{4}$$

where Q (m^3/s) is the volumetric flow rate of the pollutant ($Q=v_{air}WH$), and C_{out}=C(x = L).

The experimental data is in good agreement with the L-H model as shown in Fig. 2 which indicates that the L-H model is suitable to be used to in this research. The k and K obtained from the intercept and slope of the trend line in Fig. 2 are 5.75×10^{-4} (mg/m^2s) and 7.593 (m^3/mg), respectively. The accuracy of the trend line is also reflected by the accuracy of the initial NO concentration which is addressed in the first column of the Table 1.

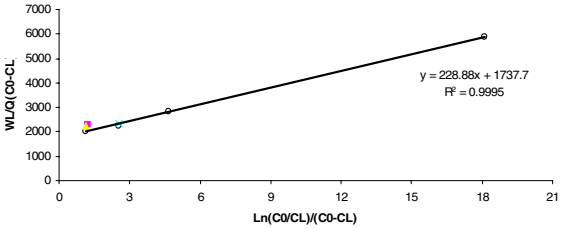

Fig. 2 Plot of NO photocatalytic degradation using L-H model

5 Discussion

To assess the effect of the light source, experiments with UVA have been executed as well. The obtained conversion rate is then 52.6%, with as experimental conditions: initial NO concentration: 1.0 ppm; flow rate: 3.0 L/min; UVA light intensity: 10.0 W/m^2; relative humidity: 50%; room temperature (21.5°C) which is in accordance with [3]. The results indicate that the carbon-doped TiO_2 has a similar effect as the undoped TiO_2 in UV light region, which is more than three times of that of the visible light with the same experimental conditions.

The PCO reactor size also plays an important role in PCO study. The present reactor has a fixed surface size with the height, the distance between the paralleled surface of the testing sample and the covering glass plate, can be adjusted by the

screws in the bottom of the reactor. In the present study, 3 mm is used as a standard height. Equation (4) shows the final concentration only relates with the initial concentration with a fixed volumetric flow rate. To study the influence of the reactor height, tests were deployed shown in Fig. 3. The results indicate that the PCO has no relation with the reactor height. To improve the PCO rate, one method is to increase the contact area of the sample with the pollutant, e.g. to increase the surface area of the photocatalyst.

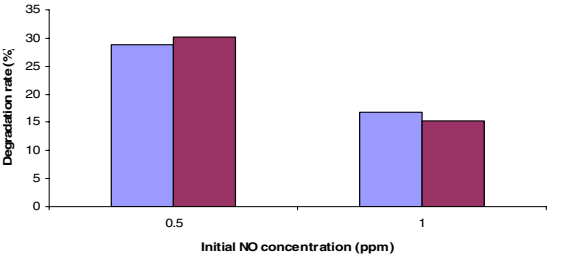

Fig. 3 PCO results. Reactor height: Initial NO concentration (0.5 ppm): 5 mm (right) and 3 mm (left); initial NO concentration (1.0 ppm): 5 mm (right) and 3 mm (left)

6 Conclusions

With the application of plasterboard as substrate and carbon-doped TiO_2 as photocatalyst and NO as pollutant, PCO has been proved to be a promising air purifying technology for indoor air quality improvement in the present research.

The kinetic L-H model is applied to describe the PCO reaction mechanism. A mathematical expression is obtained to express the concentration change in the reactor. The L-H model turns out to agree well with the experimental results.

The study of the reactor shows that only the surface area of the reactor influences the PCO rate. The effect of the carbon-doped TiO_2 is studied and UV light has a rather better PCO effect than that of visible light. So how to use the UV light in indoor conditions will be an important topic in the next research stage.

Acknowledgments. The authors gratefully express their appreciation to Dipl.-Ing. M. Hunger, Dipl.-Ing. G. Hüsken, and Ir. A.C.J.de Korte for their help with the measurement and analysis. Moreover, the authors wish to express their thanks to the European Commission (I-SSB Project, Proposal No.026661-2) and the following sponsors of the research group: Bouwdienst Rijkswaterstaat, Rokramix, Betoncentrale Twenthe, Graniet-Import Benelux, Kijlstra Beton, Struyk Verwo Groep, Hülskens, Insulinde, Dusseldorp Groep, Eerland Recycling, ENCI, Provincie Overijssel, Rijkswaterstaat Directie Zeeland, A&G maasvlakte, BTE, Alvon Bouwsystemen, and V. d. Bosch Beton (chronological order of joining).

References

1. ISO 22197-1. Fine ceramics (advanced ceramics, advanced technical ceramics) ÷ Test method for air purification performance of semiconducting photocatalytic materials ÷ Part 1: Removal of nitric oxide, 1st edn. (2007)

2. Ao, C.H., Lee, S.C.: Enhancement effect of TiO_2 immobilized on activated carbon filter for the photodegradation of pollutants at typical indoor air level. Appl. Catal. B-Environ. 44, 191–205 (2003)
3. Blöß, S.P., Elfenthal, L.: Doped titanium dioxide as a photocatalyst for UV and Visible Light. In: Proceedings International RILEM Symposium on Photocatalysis, Environment and Construction Materials TDP, Florence, Italy (2007)
4. Carneiro, J.O., Teixeira, V., Portinha, A., et al.: Study of the deposition parameters and Fe-dopant effect in the photocatalytic activity of TiO_2 films prepared by dc reactive magnetron sputtering. Vacuum. 78, 37–46 (2005)
5. Choi, W., Termin, A., Hoffmann, M.R.: The role of metal ion dopants in quantum-sized TiO_2: correlation between photoreactivity and charge carrier recombination dynamics. J. Phys. Chem. 98, 13669–13679 (1994)
6. Fujishima, A., Honda, K.: Electrochemical photolysis of water at a semiconductor electrode. Nature 238, 37–38 (1972)
7. Hoffmann, M.R., Martin, S.T., Choi, W., et al.: Environmental applications of semiconductor photocatalysis. Chem. Rev. 95, 69–96 (1995)
8. Hunger, M., Brouwers, H.J.H.: Self-cleaning surfaces as an innovative potential for sustainable concrete. In: Proceedings international conference excellence in concrete construction-through innovation, London, United Kingdom, September 9-10 (2008)
9. Hüsken, G., Hunger, M., Brouwers, H.J.H.: Comparative study on cementitious products containing titanium dioxide as photo-catalyst. In: Baglioni, P., Cassar, L. (eds.) Proceedings International RILEM Symposium on Photocatalysis, Environment and Construction Materials-TDP 2007, pp. 147–154. RILEM Publications, Bagneux (2007)
10. Kuo, C.S., Tseng, Y.H., Huang, C., et al.: Carbon-containing nano-titania prepared by chemical vapor deposition and its visible-light-responsive photocatalytic activity. J. Mol. Catal. A-Chem. 270, 93–100 (2007)
11. Obee, T.N., Brown, R.T.: TiO_2 photocatalysis for indoor air applications: effects of humidity and trace contaminant levels on the oxidation rates of formaldehyde, toluene, and 1, 3-butadiene. Environ. Sci. Technol. 29, 1223–1231 (1995)
12. Turchi, C.S., Ollis, D.F.: Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack. J. Catal. 122, 178–192 (1990)