NATIONAL CENTER FOR SCIENTIFIC RESEARCH "DEMOKRITOS"

Institute of Materials Science "Nanofunctional and Nanocomposite Materials Lab"

LABORATORY MEASUREMENTS OF PHOTOCATALYTIC PERFORMANCE OF THE SAMPLES FROM ABOLIN COMPANY

ISO 22197-1



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CONTENT

1.	Introduction	2
2.	Experimental evaluation	2
3.	Experimental results	4
4.	Conclusion	8
5.	References	9

1. Introduction

Removal of air pollutants from the atmosphere including nitrogen oxides NOx is a typical application of photocatalysis [1] that has been evolved in a standard procedure for photocatalytic activity evaluation of the materials. The present report concerns the measurement results on photocatalytic activity of several photocatalytic samples provided by ABOLIN Co, Greece. The samples were investigated for degradation of NO pollutant at the "Nanofunctional and Nanocomposite Materials Lab", Institute of Materials Sciences, NCSRDemokritos. The study includes:

- measurements of the NO monoxide,
- measurements of the NO2 dioxide,
- determination of NOx removal.

2. Experimental evaluation

The list of the investigated samples is presented in Table 1. The dimensions of the test pieces used were approximately 90 mm x 46mm x 5 mm. The samples were prepared from cement. Their surfaces were covered with photocatalytic coating from commercial active cool material.

Table 1. List of the investigated samples

N	Sample designation	Comments
1	AB-ACW4	with active cool coating
2	AB-ACW5	with active cool coating
3	AB-ACW6	with active cool coating

The applied evaluation method concerns the air purification performance of photocatalytic materials using a standard procedure based on ISO 22197-1 [2] by exposing a test piece to model polluted air under illumination by ultraviolet (UV-A) light. Nitric oxide (NO) is chosen as a typical air pollutant that gives nonvolatile products on the photocatalyst surface. The test piece placed in a flow-type photoreactor is activated by UV illumination. NO is adsorbed on the surface of photocatalyst and is converted to nitrogen dioxide (NO2) and then to nitrate ions (NO3"). During the measurement procedure, the concentrations of NO, NO2 and NOx (NOx = NO+NO2) are recorded using chemiluminescent analyzer. The air purification performance of the catalysts is determined from the amount of the net removal of nitrogen oxides (NOx). It can be expressed as a difference: NO removed - NO2 formed. The adsorption and desorption of NO by the test pieces (not due to photocatalysis) is evaluated by tests in the dark.

The short description of photocatalytic reactor operation is given thereafter. The NO gas is supplied from a gas bottle and is diluted with air. Two mass flow controllers are used to create a suitable degree of humidity of the diluted gas. Air controlled by the first controller passes through a humidifier with saturated steam and then it is mixed with the dry air controlled by the second controller. Then, the air enriched with moisture is mixed with NO and passes through the photocatalytic reactor. The concentrations of NO, NO2 and NOx gases are recorded in real time by chemiluminescent radiation analyzer and are displayed on the computer screen.

The investigated samples from Abolin Co were exposed to model air containing lppm nitric oxide (NO). The NO gas flow rate over the samples was approximately 3L/min. The starting concentration of NO2 was ~ Oppm. The photocatalytic tests were performed at room temperature (298°K) and relative humidity 50%. The photocatalytic activity of the samples was evaluated under UV-A light illumination with intensity 10 W/m² for 60 minutes in overall. The illumination was repeated 3 times for 20 min (without test piece preirradiation, after 3 day irradiation and after 7 day irradiation).

3. Measurement results

The measurement results are presented in Fig. 1, Fig. 2 and Fig. 3 for the samples AB-ACW4, AB-ACW5 and AB-ACW6, respectively. Every figure for each sample gives the recorded data without preliminary UV-A irradiation (Fig. 1-3 a), after 3day (Fig. 1-3 b) and after 7 day UV-A irradiation (Fig 1-3 c) of the samples.

Initially, an adsorption-desorption equilibrium of NO (NO_X) gases at \sim 1 ppm was reached over the photocatalyst in the dark. A shallow "dive" which represents the adsorbed quantity of NO on the photocatalyst was recorded for all the samples.

For all the samples after 3 and 7 day irradiation the NO oxidation activity increased considerably. The NO and NO_X concentration dropped sharply at the first moment and remained practically constant till the end of the illumination that



A b

Fig. 1. Recorded gas concentrations under UV irradiation for AB-ACW4 sample.



Fig. 2. Recorded gas concentrations under UV irradiation for AB-ACW5 sample.



Fig. 3. Recorded gas concentrations under UV irradiation for AB-ACW6 sample.

evidences the absence of saturation of the samples by solid reaction products. The NO2 concentrations exhibited practically constant behavior after a rapid initial increase. It should be mentioned, that the NO oxidation activity for the samples after 7 day irradiation is somewhat lower in comparison with the results received after 3 day irradiation. This can be explained by a slight soiling of the photocatalyst surface that decreases the number of active sites on its surface.

The detailed measurement data are shown in Table 2. There, the results for gas concentrations are presented in the beginning of the UV illumination after an abrupt alteration in the gas concentrations and in the end of the illumination interval.

Sample	Number of meas- ure ment	NO concentration (ppm)		NO2 concentration (ppm)		NOx concentration (ppm)	
		Start	End	Start	End	Start	End
AB-A	1	0.92	0.92	0.02	0.04	0.94	0.96
CW4	2	0.59	0.69	0.18	0.20	0.77	0.89
	3	0.70	0.77	0.16	0.18	0.86	0.95
AB-A	1	0.90	0.87	0.01	0.05	0.91	0.92
CW5	2	0.61	0.73	0.17	0.17	0.78	0.90
	3	0.68	0.80	0.14	0.14	0.82	0.94
AB-A	1	0.93	0.93	0.02	0.03	0.95	0.96
CW6	2	0.57	0.72	0.18	0.18	0.75	0.90
	3	0.57	0.77	0.21	0.17	0.78	0.94

Table 2. Measurement results in the beginning and in the end of the illumination interval.

4. Conclusion

The three investigated samples exhibited practically the same photocatalytic activity for oxidation of NO air pollutant.

After the direct exposure to NO pollutant under UV irradiation without preliminary UV irradiation, the examined samples revealed photocatalytic NO oxidation power. After beginning the illumination, the NO concentration reached the values of 0.90-0.93 ppm and then slightly decreased with time. The NO2 production was extremely low (0.01-0.02 ppm) and showed smooth increase with time attaining values around 0.03-0.05 ppm after the irradiation time of 20 min. • After the UV irradiation of 3 days, the NO oxidation power of the samples was significantly improved. Once the UV illumination started:

- the NO concentration decreased abruptly from 1 ppm to 0.56-0.57 ppm and then maintained practically constant around 0.72-0.76 ppm;

- the NO₂ concentration increased from 0 ppm to approximately constant value of 0.17-0.20 ppm;

- the NOx values exhibited sharp decrease from 1 ppm to 0.76 ppm and stabilised at approximately 0.89-0.94 ppm.

After the UV irradiation of 7 days, the NO oxidation activity decreased to some extent that can be explained by soiling of the photocatalyst surface. Thus, the equilibrium values of gas concentration in the end of illumination interval were around 0.77-0.80 ppm, 0.14-0.17 ppm and 0.94-0.95 ppm for NO, NO₂ and NOx gases, respectively.

5. References

[1] T. Ibusuki and K. Takeuchi, Removal of low concentration nitrogen oxides through photoassisted heterogeneous catalysis, *J. Mol. Catal.*, 88, 93-102 (1994). [2] ISO 22197 -1:2007 - Fine ceramics (advanced ceramics, advanced technical ceramics) - Test method for air-purification performance of semiconducting photocatalytic materials. Part 1: Removal of nitric oxide.