CHEMISTRY DEPARTMENT

NATIONAL RESEARCH COUNCIL

UNIVERSITY OF FERRARA

ISTITUTO PER LA SINTESI ORGANICA E LA FOTOREATTIVITA'

Sezione di Ferrara

TECHNICAL REPORT ON THE PHOTOCATALYTIC ACTIVITY OF VITREOUS MATERIALS MANUFACTURED FROM SICIS - THE ART FACTORY S.r.l.

NO_x ABATEMENT

Ferrara, 2/12/10

The present report contains results about experimental tests aiming to evaluate of the photocatalytic activity of vitreous materials in the NO_x removal from gaseous phase. Samples have been received from SICIS- The Art Factory S.r.l.

Introduction

Titanium Dioxide is a semiconductor material able to absorb UV and, to less degree, visible light. In general, when illuminated with light whose energy is larger than the semiconductor band gap, electrons are promoted to the conduction band and a hole (h^+) is left in the valence band.
Holes can react with a water molecule to give a highly reactive hydroxyl radical whereas electrons have enough reduction power to can react with oxygen molecules to give superoxide anion (O_2^-), as show on the following equations

$$H_2O + h^+ \longrightarrow OH\bullet + H^+$$

$$O_2 + e^- \longrightarrow O_2\bullet^-$$

These radicals contribute to an efficient oxidation and mineralization of organic compounds to CO_2 and water and can also convert inorganic species such as nitrogen and sulfur oxides to less noxious compounds (nitrates and sulfates)[1-6]. Another interesting aspect of TiO_2 photocatalysis is connected with an antibacteric, antimicrobic and antimould action as amply documented in the literature[7,8].

References

1) Ollis, D.; F. Pelizetti E; Serpone N. Environ Sci. Technol. 1991, 25, 1523.
2) Uccida, H.; Itoh, S.; Yoneyama, H. Chem. Lett. 1993, 1995.
3) Heller, A. Acc. Chem. Res. 1995, 28, 503.
4) Sitkiewitz, S.; Heller, A. New J. Chem 1996, 20 233.
5) Watanabe, T.; Kitamura, A.; Kojima, E.; Nakayama, C.; Hashimoto, K.; Fujishima, A.; In Photocatalytic Purification and Treatment of Water and Air; Ollis D. E., Al-Ekabi, H.; Eds; Elsevier: New York, 1993, 747.

6) Matsubara, H.; Takada, M.; Koyama, S.; Hashimoto, K.; Fujishima, A. Chem Lett. 1995, 767.
7) Negishi, N.; Iyoda, T.; Hashimoto, K.; Fujishima, A. Chem Lett. 1995, 841.
8) Sunada, K.; Kikuki, Y.; Hashimoto, K.; Fujishima, A. Environ Sci Technol, 1998, 32, 726.

SAMPLES DESCRIPTION

The following Table reports the samples received with the denomination that identified them and that will be used in the present report.

Samples under study	Denomination
Iridium Collection	**IC**
Iridium Collection with photocatalytic coat	**IC+TiO_2**
Glimmer Collection	**GC**
Glimmer Collection with photocatalytic coat	**GC+TiO_2**

The sample aspect is that of a mosaic with pieces having an average dimension of 1.3 cm x 1.3 cm. Figure 1 shows a picture of the samples analyzed in the abatement of NO_x . It can be noted that the photocatalytic layer on the samples is characterized by iridescence.

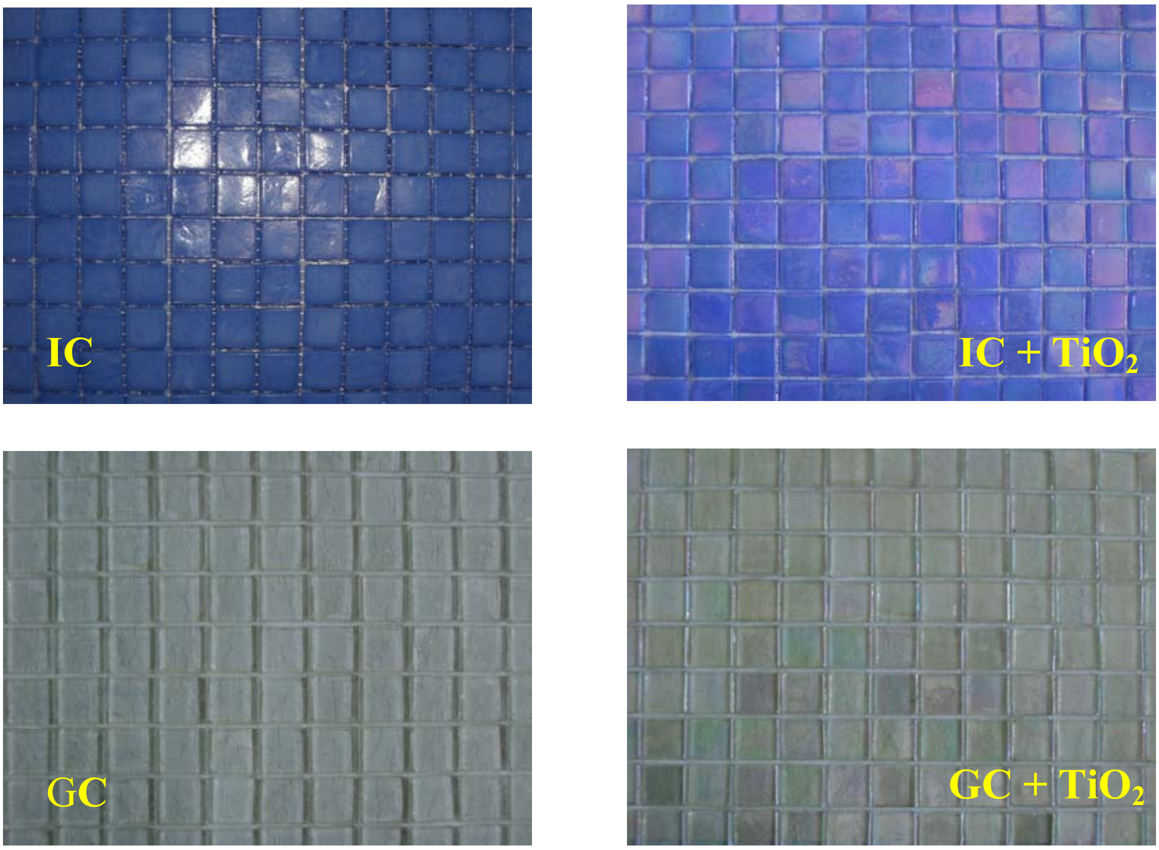
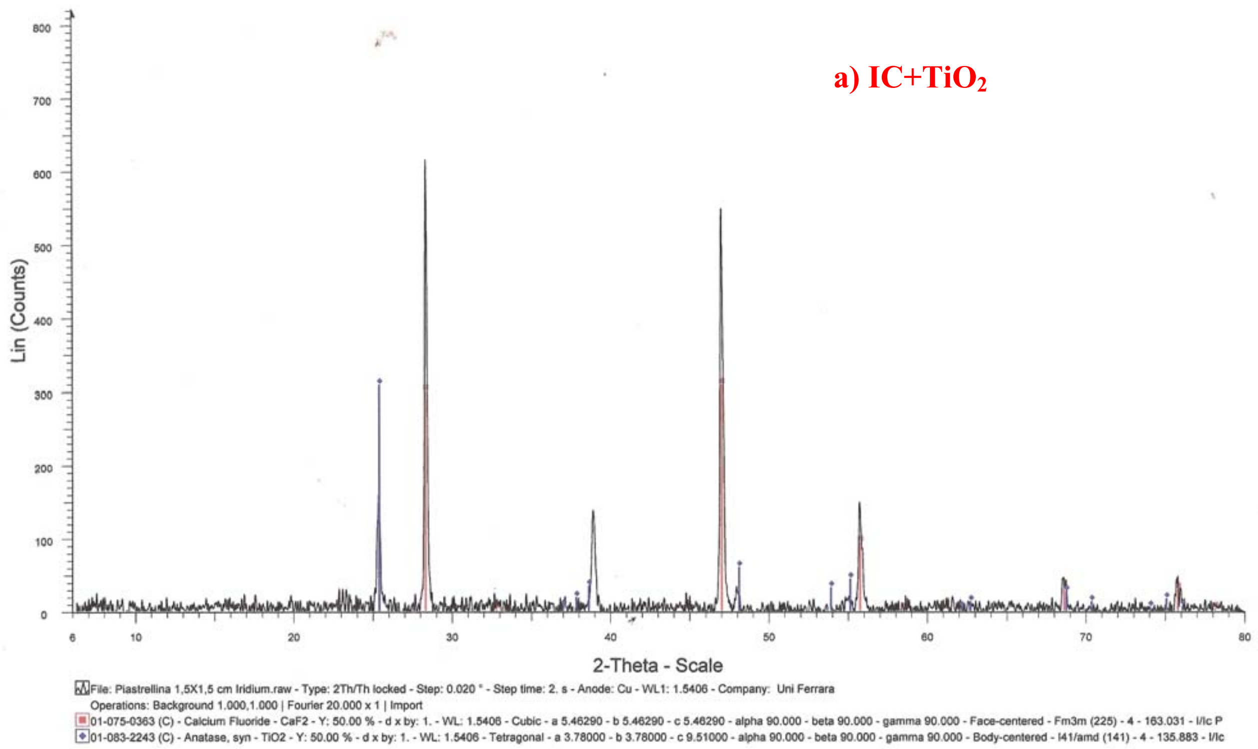


Figure 1 Pictures of the samples examined in photocatalytic tests of NO_x abatement

Figure 2 (a and b) shows XRD spectra of samples with photocatalytic coating. It is clearly seen that at the surface of sample IC+TiO_2 another compound is present which is possibly identified as CaF_2. Additionally, in both examined samples, TiO_2 is present in the form of anatase.



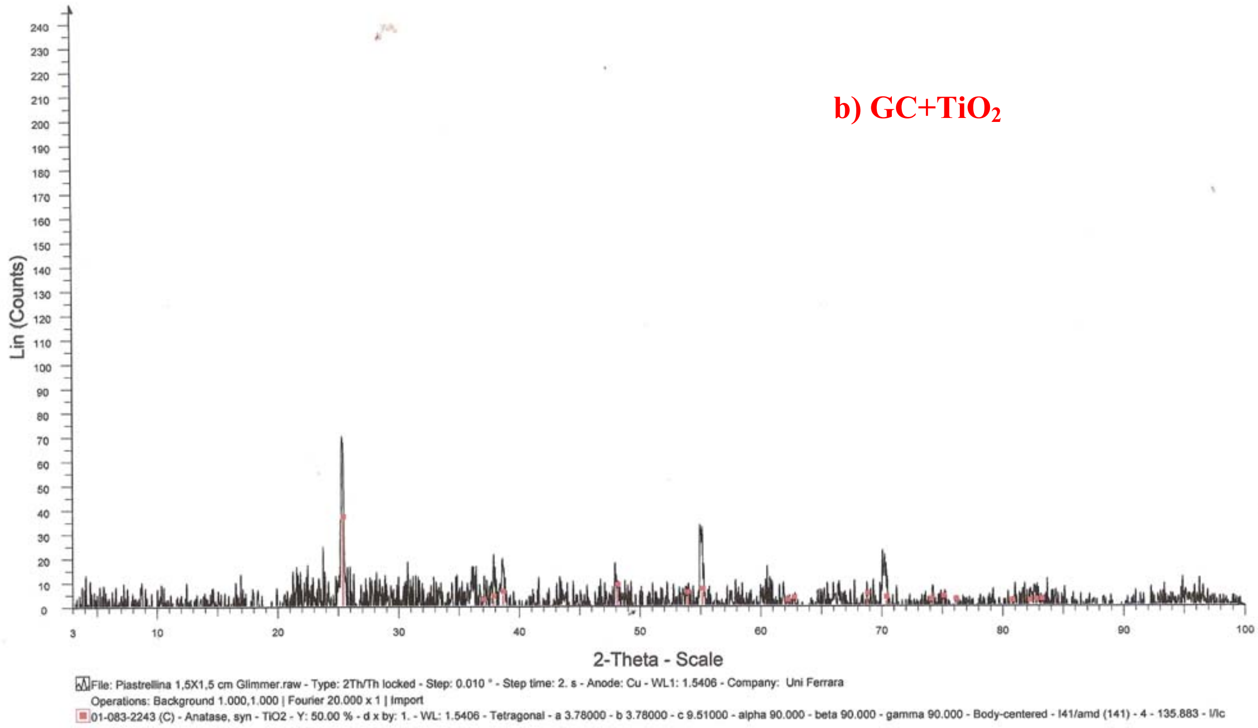


Figure 2 XRD spectrum of samples IC+TiO_2 (a) and GC+TiO_2 (b)

EXPERIMENTAL RESULTS

Experimental procedure for the assessment of nitrogen oxides abatement

Measurements of NO_x abatement upon illumination have been carried out according to the “continuous flux” method as reported in the UNI-11247-2007 standard.
A Nitrogen Oxides Analyzer, Model AC32M from Environnement S.A. was used for the measurements. Experimentally, air containing 0.55 ppm NO_x (0.15 ppm NO_2 + 0.4 ppm NO) is made to flow at a rate of 1 L/min through a 3 L reactor containing the sample (64 cm^2). The temperature inside the reactor was maintained at 26-28°C and humidity is controlled in the range 45-60%.
When the concentration of NO_x is stable in the dark (C_B), the sample is illuminated by a 300 W Osram Vitalux lamp, placed at such a distance from the sample that ensures a radiant power of 20 W/m^2 as measured by a Macam UV203 radiometer in the range 300-400 nm. Irradiation is continued until the NO_x concentration reached a stable value (C_L).
Photocatalytic activity (A_F), reported as m/h, is calculated by the following equation

$$A_F = \frac{C_B - C_L}{C_B} \times \frac{F}{S} \times I$$

where
C_B and C_L represent stable concentrations in the dark and under illumination, respectively.
S is the sample geometric area in m^2
F is the gas flux in m^3/h
I is the dimensionless light intensity given as ($I = 1000/I'$), where 1000 (W/m^2) refers to the average irradiance of light in a sunny day in July and I' is the lamp intensity (W/m^2).

ISOF-CNR and Chemistry Department-University of Ferrara,* Via L. Borsari 46 –*Ferrara-Italy

Photocatalytic activity

In agreement with a vast literature, between the two nitrogen oxides constituting NO_x, i.e. NO and NO_2, the first one is not appreciably adsorbed on the photocatalyst. The second species, instead, is adsorbed in the dark and the degree of adsorption depends on the acid-base properties of the surface and on humidity. It then turns out that NO is a better probe for the assessment of photocatalytic activity since its removal from air is essentially due to photocatalysis.

In the following Table 1 are shown the results of tests on the photoactivity (A_F) of the samples examined toward removal of NO_x from air. In the same Table are also shown the individual photoactivity values for the abatement of NO_2 and NO.

Experimental Parameters:

Reactor Volume: 3 litres

Gas flow: 0.06 m^3/h

Geometric area of sample: 0.0064 m^2

Light Intensity: 20 W/m^2

Table 1 Photocatalytic activity (A_F) based on UNI-11247 Standard

Sample \ A_F (m/h)	NO_x	NO_2	NO
IC	16.4	37.5	8.4
IC+TiO_2	24.4	60.9	10.8
GC	27.7	15.5	32.3
GC+TiO_2	34.8	22.9	39.3

In the elaboration of experimental results, it is to be considered that, complete removal of each species would correspond to an activity A_F of **468.7 m/h.**

In Table 2 the results are expressed as percent removal of NO_x.

ISOF-CNR and Chemistry Department-University of Ferrara,* Via L. Borsari 46 –*Ferrara-Italy

Table 2 Photocatalytic activity as percent abatement

Sample \ A_F (%)	NO_x	NO_2	NO
IC	3.5	8.0	1.8
IC+TiO_2	5.2	13.0	2.3
GC	5.9	3.3	6.9
GC+TiO_2	7.4	4.9	8.4

Conclusions:

Results of photoactivity tests that have been carried out according to the method of continuous gas flux as described in UNI-11247-2007, have shown that coating of the glass material with TiO_2 leads to an enhancement of the photocatalytic activity compared with the reference materials.

It is found, additionally, that sample GC+TiO_2 features a higher activity than IC+TiO_2 in the abatement of NO. The difference can be ascribed to the simultaneous presence of CaF_2 in sample IC+TiO_2.

Dr. Rossano Amadelli **Dr. Luca Samiolo**

Ferrara, 2/12/10