**Military Technical College
Kobry Elkobbah, Cairo,
Egypt.**

C.E.E. 2006

**3rd International Conference
On
Chemical & Environmental
Engineering**

PHOTOCATALYTIC DEGRADATION OF THE POLYCYCLIC AROMATIC HYDROCARBON "ANTHRACENE" IN WATER USING UV-IRRADIATION AND THIN-LAYERED TRANSITION METAL OXIDE PHOTOCATALYSTS

Aboul-Gheit A. K. [*], Mahmoud S. A. [*] and Moustafa Y. M. [*]

ABSTRACT

TiO$_2$, ZnO and mixed TiO$_2$+ZnO photocatalysts in the form of thin layers mounted on 2.5 x 2.5 cm glass sheets were prepared and tested for the photocatalytic degradation of 25 ppm anthrecene in its aqueous solution using a medium-pressure 6W-UV lamp irradiating at a wave length of 254 nm as an irradiation source and a reactor made of silica glass. Analysis of the produced intermediates and the remaining anthracene after consecutive irradiation periods was achieved mainly by HPLC and GC/MS spectroscopy. The catalysts were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The activities of the current photo-catalysts were found to be in the order: TiO$_2$ > ZnO > TiO$_2$/ZnO. The same intermediates formed in the photodegradation of anthracene using TiO$_2$ and ZnO catalysts are produced, whereas using the TiO$_2$/ZnO catalyst most of these intermediates disappear, probably due to difference in the adsorption/desorption behaviours of these catalysts. Organic acids were the predominant intermediates on all catalysts; they are the most resistive against photocatalytic degradation.

KEY WORDS

Photocatalytic degradation, transition metals, TiO$_2$, ZnO, UV irradiation.

---

[*]   Egyptian Petroleum Research Institute.

1. INTRODUCTION

Semiconductor surfaces when exposed to light having the suitable band gap energy, result in photo-excitation of the *valence band electrons* to the *conduction band*, leaving holes or electron vacancies. These, under certain controlled conditions, can serve as powerful oxidizing agents at the solid-liquid interface. This process is developing into an environmental technology for the destruction of many organic and some inorganic pollutants in industrial waste waters.

Titanium dioxide (TiO_2) is a semiconductor photocatalyst with a band-gap energy of 3.2 eV. When this material is irradiated with photons of wave lengths less than 385 nm, the band gap energy is exceeded and an electron is promoted from the valence band (vb) to the conduction band (cb). The resultant electron-hole pair has a lifetime in the space-charge region that enables its participation in chemical photo-reactions as postulated in the steps shown below:

$$TiO_2 + h\nu \longrightarrow e^-_{cb} + h^+_{vb} \tag{1}$$

$$h^+_{vb} + {}^-OH_{ad} \longrightarrow {}^\bullet OH_{ad} \tag{2}$$

$$e^-_{cb} + O_2 \longrightarrow {}^\cdot O_2{}_{ad} \tag{3}$$

Hydroxyl radicals (equation 2) and super-oxide ions (equation 3) are the highly reactive species which will oxidize organic compounds adsorbed on the catalyst surface.

Photo-degradation catalysts can be used as pellets, extrudates, balls, etc. However, powdered catalysts acquire higher activities than the formed ones, since intra-particle diffusion limitation is minimized. However, recently, thin-layered photocatalysts have been prepared and used for degrading toxic organic pollutants in water. Although powdered catalysts acquire higher photo-degradation activities than the formed ones, they show still lower activities than the thin layered catalysts beside encountering serious problems in separating them from the treated water. A few work dealing with thin-layered photocatalysts has appeared [1-3]. Pal and Sharon have prepared TiO_2 thin films [4], ZnO thin films [5] and Fe_2O_3 thin films [6]. Sudnik et al. [7] have prepared Ag^+ on TiO_2 films. Mishra et al. [8] prepared SnO_2 thin film, whereas Ceccato and Carturan [9] prepared vanadium thin films. Leite et al. [10] prepared $SrTiO_3$ thin films.

2. EXPERIMENTAL

TiO_2, ZnO and mixed TiO_2/ZnO photocatalysts were prepared in the form of thin layers mounted on a 2.5 x 2.5 cm glass sheet. They were prepared using a sol-gel technique and tested for the photocatalytic degradation of anthrecene in its aqueous solution. In case of the TiO_2 and ZnO catalysts, the preparation was carried out via depositing six thin layers of the metal oxide, while in case of the mixed TiO_2/ZnO catalyst, three layers of TiO_2 and three layers of ZnO were deposited consecutively.

The pollutant used was always anthracene, which is a polycyclic aromatic hydrocarbon known by its carcinogenicity. Anthracene was dissolved in distilled water in a concentration of 25 ppm (maximum dissolution available). The radiation source was a medium pressure 6 W-UV lamp irradiating at 254 nm and the reactor was made of silica glass in order to be totally penetrated by UV irradiation. Irradiated polluted water samples were withdrawn for analysis using HPLC chromatography at irradiation-time intervals of 2 min during the initial period up to 10 min, beyond which the irradiation intervals were increased to 5 min or even to 10 min. The HPLC stationary phase was a long chain alkane hydrocarbon and the mobile phase was acetonitrile/water mixture pumped at a rate of 1.0 cm^3 min^{-1}. The intermediates obtained were identified via injecting all expected oxidation and oxidative degradation products Gas chromatography was helpful for checking and analyzing some lighter photo-intermediates, particularly when the GC/MS combination was applied.

3. RESULTS AND DISCUSSION

Thin-layered photocatalysts are generally superior over all types of catalysts possessing different forms, via acquiring superior photodegradation activities in addition to excluding separation problems such as those occurring when using powdered catalysts. In presence of thin layered photocatalysts, the separation from the treated water is spontaneous, i.e., water moves while the sheets supporting the catalytic material are remaining fixed in their positions. In the authors' laboratory, the photodegradation of anthracene has been tested in aqueous solution containing a glass sheet with the dimensions: 2.5 x 3.0 cm^2. This sheet supports a thin-layered TiO_2 catalyst, weighing 0.003g TiO_2. This catalyst has been found to acquire ~5 times the photo-degradation activity of a powdered TiO_2 catalyst weighing 0.1 g. Hence, 5 x 0.1 divided by 0.003 equals 167, i.e.; it can be said that the thin-layered catalyst prepared according to our technique on a glass sheet is ~167 times as active as a corresponding powdered catalyst.

Till now a few communications concerned with thin-films of photocatalytic semiconductor transition metals have recently appeared in the literature [1-3]. However, these preparations did not yield the completely active materials, and even the prepared films have not been very strongly fixed on the supporting sheets. This fixation is industrially very important. However, our current photocatalysts are found to fulfill successfully all such requirements.

Fig.1 and Fig.2 show the data including the unconverted anthracene and the aromatic photo-oxidation products using the current thin-layered TiO_2 and ZnO photocatalyst, respectively. Although these intermediate components are qualitatively the same in Figs.1 and 2, i.e., hydroxyanthraquinone, anthraquinone, benzophenone and benzoquinone, their magnitudes in both figures are different due to difference in the catalytic activities of the TiO_2 and ZnO.

Using the ZnO catalyst (Fig.2), these intermediates are present in larger concentrations, beside their formation at longer irradiation times than on using the TiO_2 catalyst, indicating higher photodegradation activity of TiO_2. Even though, Figs.1 and 2 don't show the curves representing organic acids, which constitute an

important series of intermediates, since these acids exhibit much higher resistance to photodegradation than the cyclic intermediates. Schemes I and II may explain successive photocatalytic oxidation and oxidative degradation of anthracene in water in presence of UV irradiation, atmospheric air and the current catalysts.
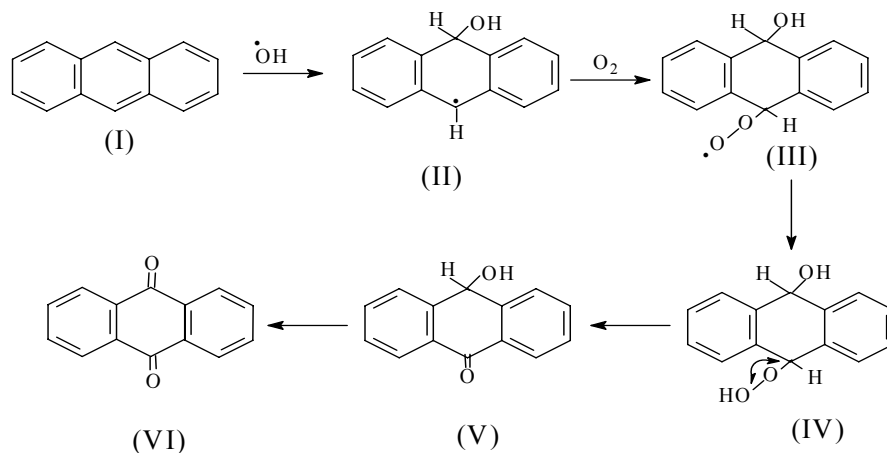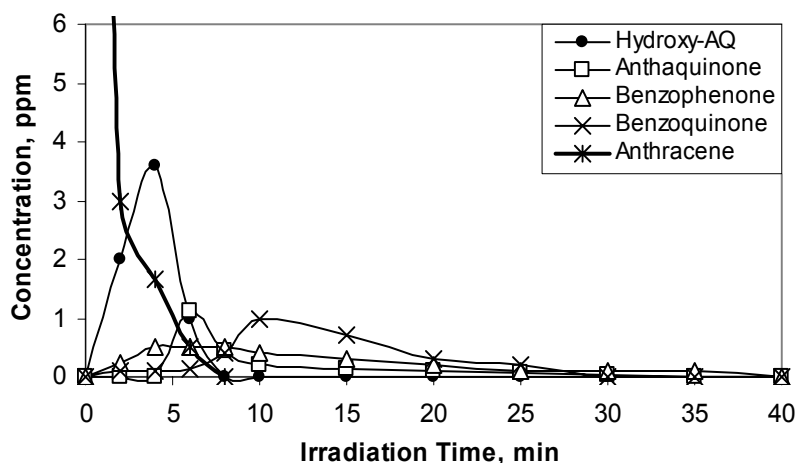

Scheme 1
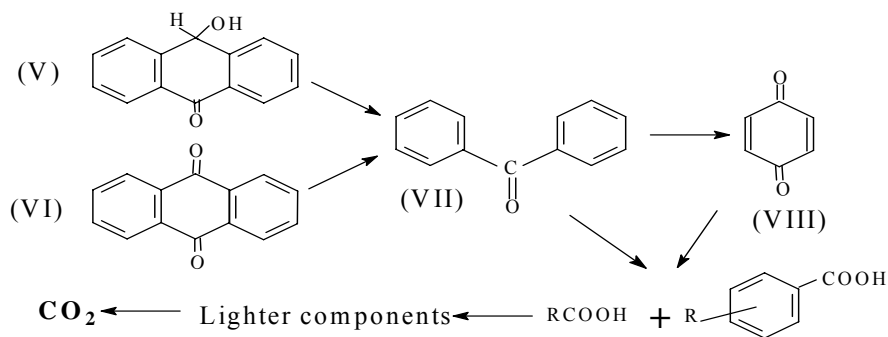
Scheme 2

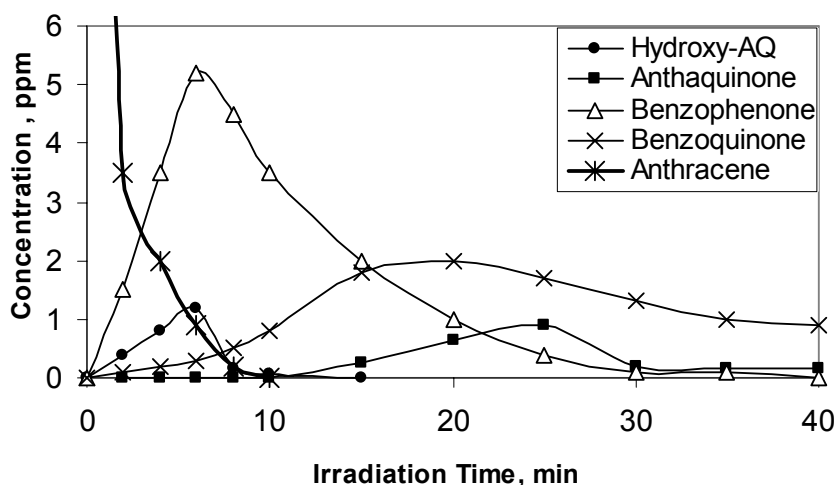Fig.1. Anthracene Photodegradation Intermediates
using TiO2 Catalyst

Fig. 2. Photodegradation Products of Anthracene
using ZnO Catalyst

It is expected that mixing half the number of TiO_2 layers to half the number of ZnO layers; the composite catalyst [TiO_2(3)/ZnO(3)] will acquire an intermediate photo-degradation activity between those of the separate TiO_2 and ZnO catalysts, speculating that the activities order will be as follows: TiO_2 > TiO_2/ZnO > ZnO. However, the actual experimental activities have been found in the following order: TiO_2 > ZnO > TiO_2/ZnO. The anthracene photodegradation products using the TiO_2/ZnO catalyst.are given in Fig.3. Evidently, the sole aromatic intermediate detected is benzoquinone during the whole irradiation time investigated (Fig.3), indicating the fast removal of hydroxyanthraquinone, anthraquinone and benzophenone after being formed, since it is impossible to believe that these three intermediates haven't been at all formed. Moreover, it is scientifically logic to consider that benzoquinone is the most stable cyclic intermediate. Benzoquinone attains a maximum of 1.0 ppm at 6 minutes irradiation time and disappears almost completely after 20 minutes, which may substantiate that it is still a weakly adsorbed compound on the mixed catalyst.
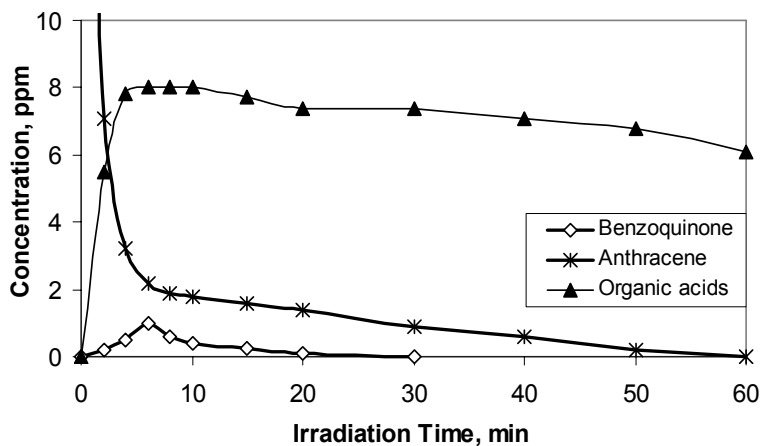
Fig. 3. Photodegradation Products of Anthracene using
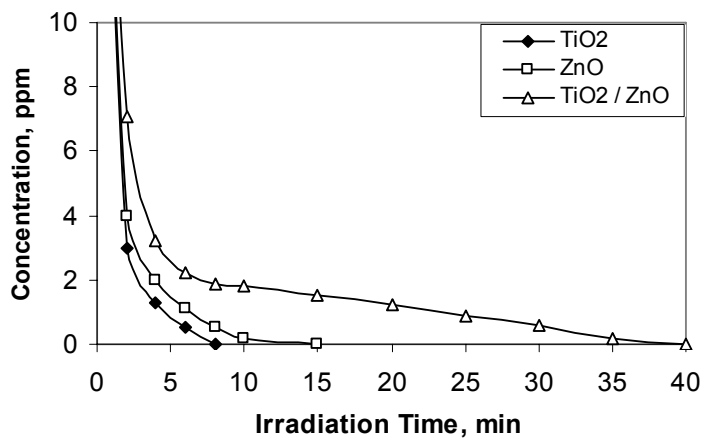the TiO2(3) / ZnO(3) Catalyst

Fig. 4. Anthracene remaining after irradiation
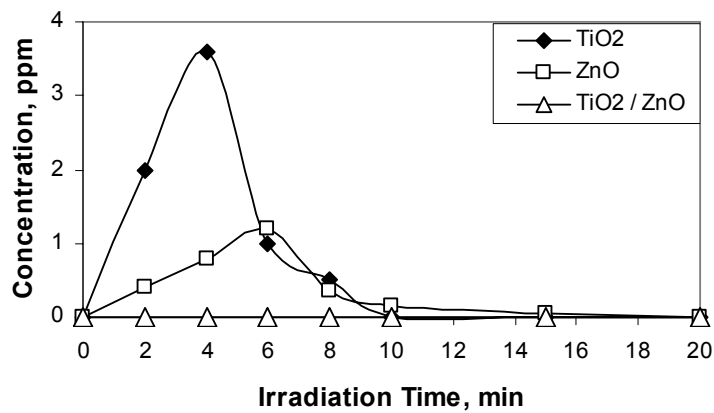using TiO2, ZnO and TiO2-ZnO Photocatalysts

Fig. 5. Hydroxyanthraquinone in Irradiated
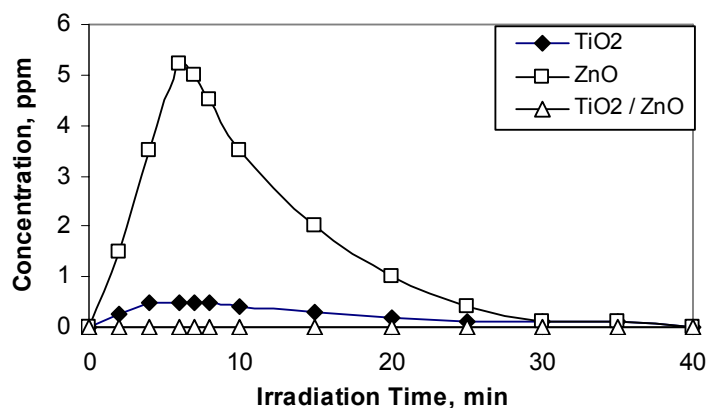Water using TiO2, ZnO and TiO2/ZnO Catalysts

Fig. 6. Benzophenone formed via the photocatalytic
degradation of anthracene using TiO2, ZnO, and
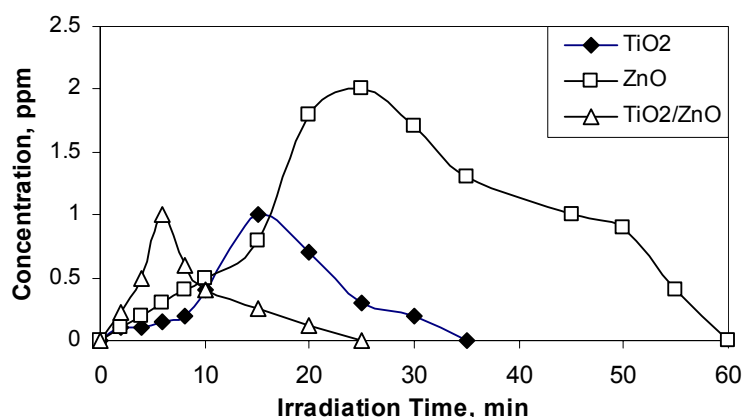TiO2/ZnO Catalysts

Fig. 7. Benzoquinone in the photodegradation
product of Anthracene using TiO2, ZnO and
TiO2/ZnO Catalyst

Figs. 4-7 compare the activity behaviour of the TiO_2, ZnO and TiO_2/ ZnO photocatalysts for producing the successive intermediates that lead, ultimately, to mineralization (CO_2 and water). Anthracene photodegradation rate (Fig. 4) show that TiO_2 > ZnO > TiO_2/ZnO. The first intermediate formed is hydroxyanthaquinone (Fig.5) followed by its further photo-oxidation to anthraquinone (Fig. 6). Figs. 4-6 show that these three intermediates are only formed on the TiO_2 and ZnO catalysts, whereas benzoquinone (Fig.7) is formed on the three current catalysts (Figs.4-7). This intermediate is formed at 6.0 min irradiation period in a relatively low concentration (1.0 ppm) using the mixed catalyst. However, using the TiO_2 and ZnO catalysts, benzoquinone comprises maxima of 1.0 and 2.0 ppm, respectively, at 15 and 25 min, respectively. This implies that the adsorption strength of benzoquinone may be the lowest on the mixed catalyst, but highest on the ZnO catalyst.
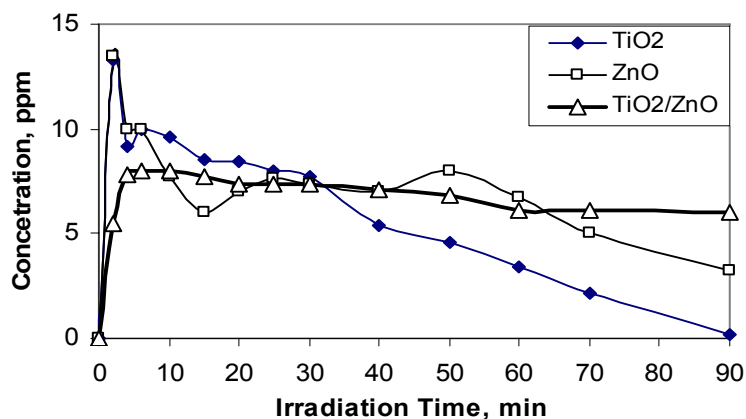
Fig. 8. Organic Acids produced during Anthracene
Photodegradation using TiO2, ZnO and TiO2/ZnO
Catalysts

Fig.8 shows that the organic acids (mainly formic and acetic acids) which are produced during the anthracene pohotodegradation are of relatively high concentrations using all current catalysts. Using the TiO_2 catalyst, these acids decrease almost linearly as a function of irradiation time till disappear at 90 min. However, using ZnO catalyst, the acids undulate in ups and downs till 50 min irradiation time, beyond which they decrease parallel to those produced using the TiO_2 catalyst till attaining 3.2 ppm at 90 min irradiation period. However, on the mixed TiO_2/ZnO catalyst, the acids concentration is slowly decreasing from 4 min up to 90 min, in an almost linear fashion, till reaching 6.0 ppm at 90 min irradiation. This behaviour may support our assumption that the cyclic intermediates are weakly adsorbed on the TiO_2/ZnO catalyst, whereas the acids are strongly adsorbed. The slow removal of organic acids may be considered the rate-determining step in the overall photocatalytic degradation of anthracene on the current catalysts.
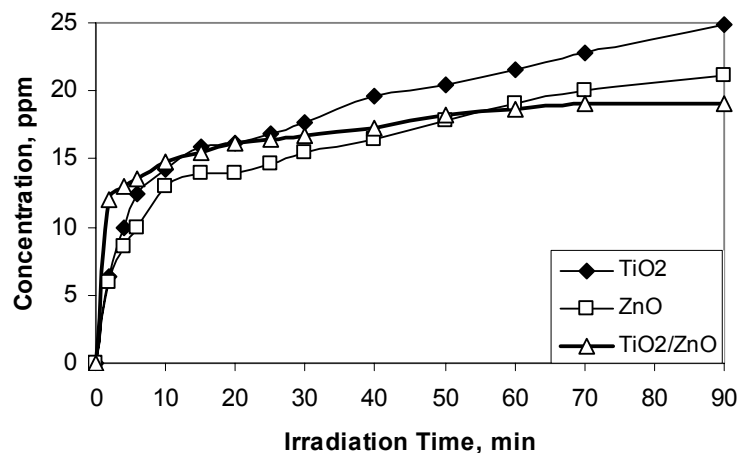

Fig. 9. Carbon dioxide evolved using TiO2, ZnO
and TiO2/ZnO Catalysts

Fig. 9 shows that the trend of total mineralization of anthracene to CO_2 and water is only decisive beyond irradiation time of 60 min, showing that photodegradation is persisting in the order: $TiO_2 >$ ZnO $>$ TiO_2/ZnO. However, at lower irradiation times (0-20 min), the mineralization order is: TiO_2/ZnO $>$ $TiO_2 >$ ZnO, which is another evidence that the TiO_2/ZnO catalyst possesses the highest adsorptive capability among the current catalysts.

The TiO_2 catalyst is well crystallized at 400$^{\text{o}}$C and its XRD pattern (Fig. 10) shows diffraction peaks which all correspond to the anatase TiO_2 form. It is known that TiO_2 crystallizes into two forms; (a) anatase and (b) rutile. The former is significantly photoactive, whereas the latter is not. Fig. 10 shows that the TiO_2 catalyst prepared in our lab doesn't include inactive rutile ingredients. However, the XRD pattern obtained for the ZnO catalyst (Fig.11) shows a very broad peak with a maximum diffraction at a 2-theta of 25$^{\text{o}}$. Even though, this ZnO catalyst acquires a relatively high photoactivity, although its XRD pattern indicates that it is amorphous. The SEM photograph for the TiO_2 catalyst (Fig. 12), shows minute crystals. which may exhibit polyhedral topology and may approach nanostructures. The branched-structure of ZnO (Fig.13) doesn't give defined crystalline structure. Even-though, the almost amorphous appearance in this photograph may disclose that it is not important for layered (thin film) catalysts to acquire well-defined crystalline structure to attain high photoactivity. Nevertheless, in Fig. 14, well-defined crystals appear allover the whole SEM plate of the TiO_2/ZnO Catalyst, although this catalyst is not more active than the others.
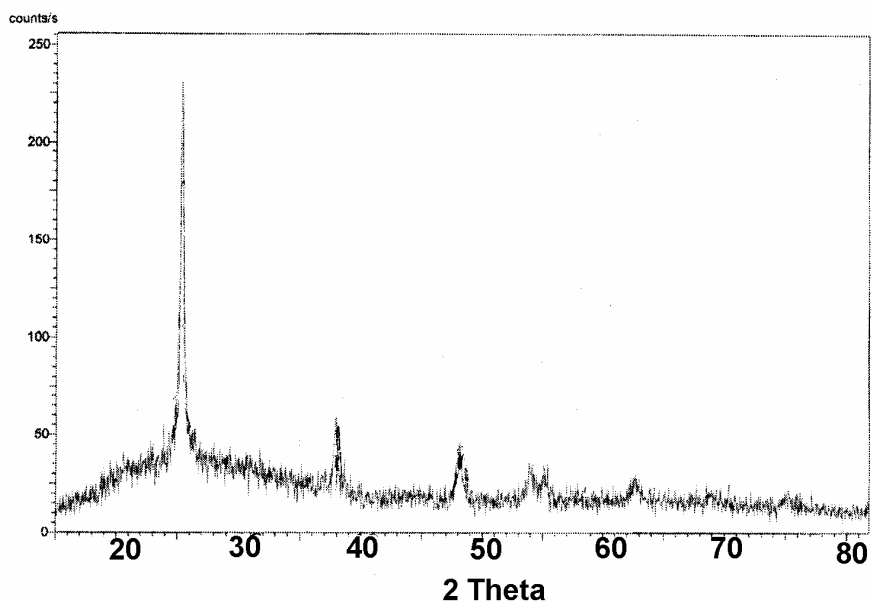

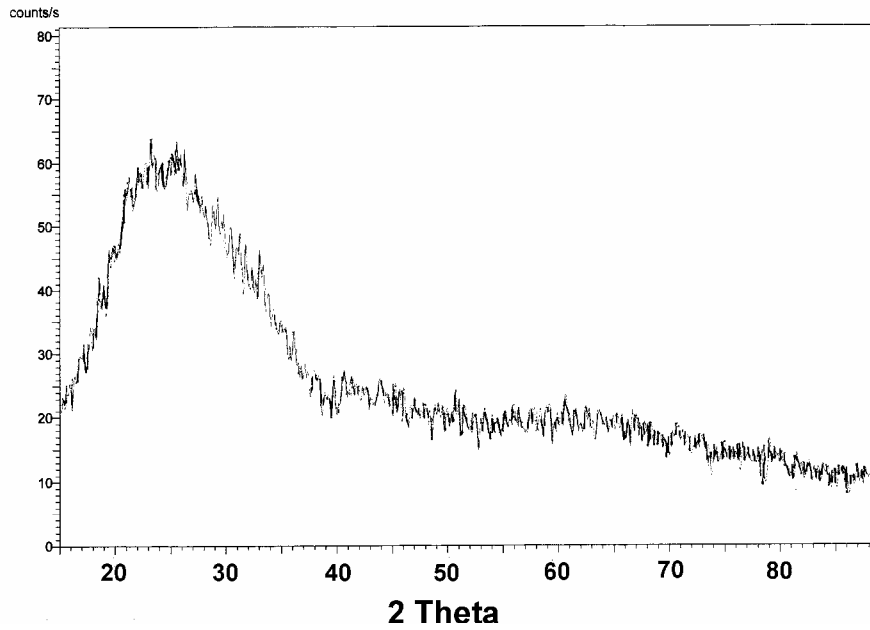Fig. 10. XRD Pattern for TiO_2 Catalyst
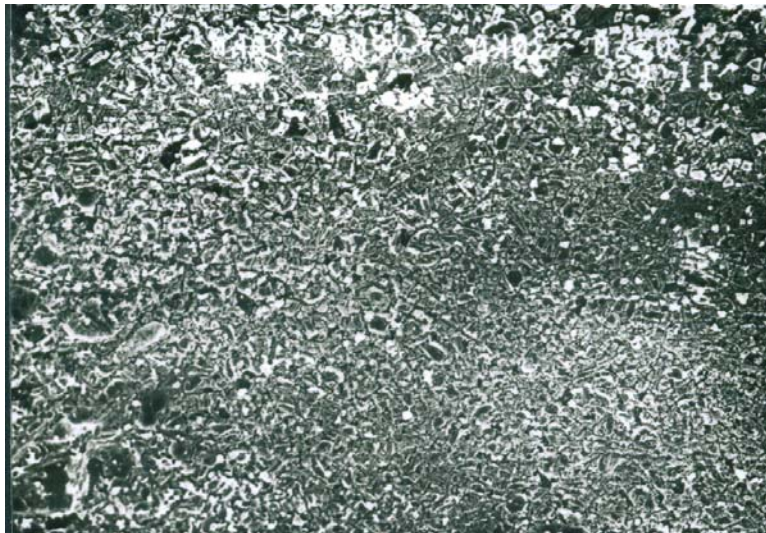
Fig. 11. XRD Pattern for ZnO Catalyst

Fig. 12.   SEM for the TiO2 thin-layered Catalyst
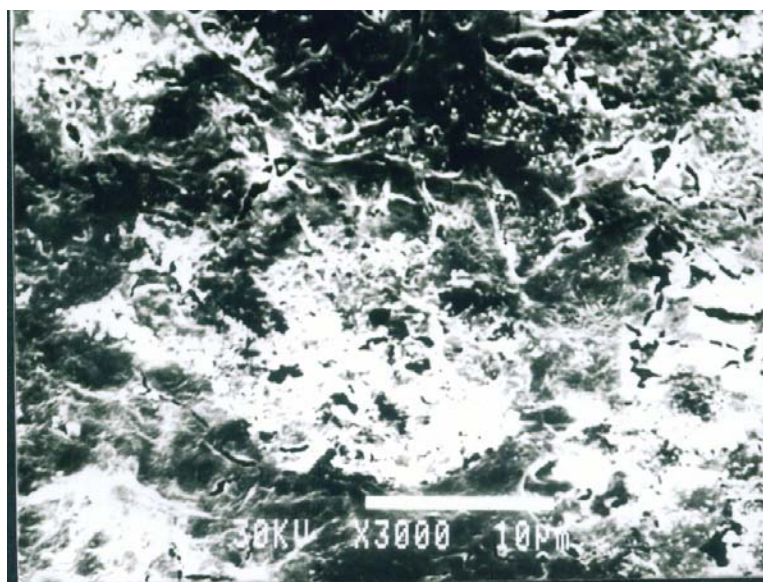(Magnification x 800)

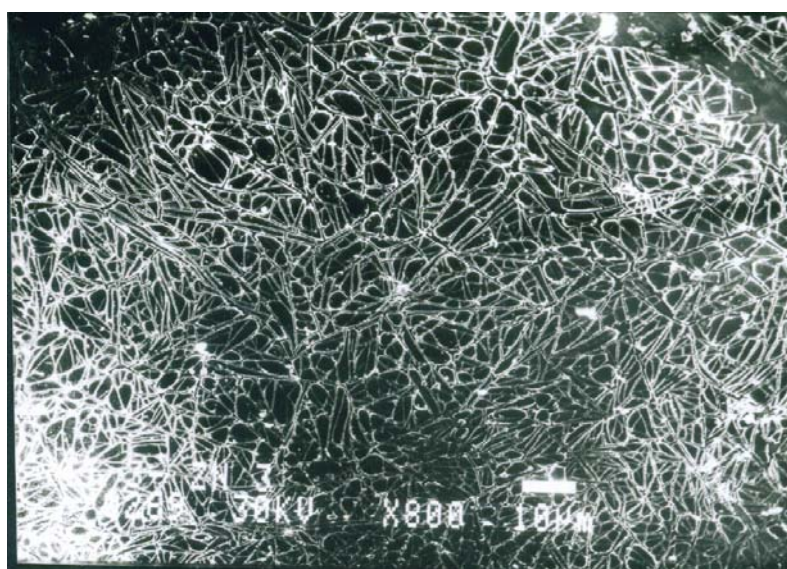Fig. 13.   SEM for the ZnO thin-layered Catalyst

Fig. 14.   SEM for the TiO2/ZnO thin-layered Catalyst

CONCLUSION

The photocatalytic degradation activities of the TiO_2, ZnO and TiO_2/ZnO catalyst for anthracene are in order: TiO_2 > ZnO > TiO_2/ZnO. However, the relatively difficult removal (photo-degradation) of organic acids can be considered the rate determining step of anthracene degradation using all current catalysts and, in particular, the mixed TiO_2/ZnO catalyst. It can be assumed that the mixed catalyst possesses a relatively weaker adsorption of the aromatic intermediates, facilitating their reaction, associated with a stronger adsorption of the acids which inhibits their photo-degradation. This adsorption/desorption phenomenon may be related to the well developed crystalline structure of TiO_2/ZnO. However, the overall photoactivities of the current catalysts are not greatly different.

REFRENCES

[1] Wu, C-H, Huang, K-S. and Chern, J-M., Ind. Eng. Chem. Res., 45, 2040-2045 (2006).
[2] Lee, J-Y., Yin, D. and Horiuchi, S., J. Chem. Mater., 17, 5498-5503 (2005).
[3] Yu, J-G., Yu, H-G., Cheng, B., Zhao, X-J., Yu, J.C. and Ho, W-K., J. Phys. Chem. B, 107, 13871-13879 (2003).
[4] Pal, B. and Sharon, H., J. Mol. Catal. A: Chem., 160, 453-460 (2000).
[5] Pal, B. and Sharon, H., J. Mater. Chem. Phys. 76, 82-87 (2002).
[6] Pal, B. and Sharon, H., J., Thin Solid Films, 379, 83-88 (2000).
[7] Sudnik, L.H., Norrod, K.L. and Rowlen, K.L., Appl. Spectr., 50, 422-424 (1996).
[8] Mishra, S., Ghanshyah, C., Ram, N., Singh, S., Bajpai, R.P. and Bedi, R.K., Bull. Mater. Sci., (25), 231-234 (2002).
[9] Ceccato, R. and Carturan, G., J. Sol-Gel Sci. Technol. (26), 1071-1074 (2003).
[10] Leite, E.R., Mastelaro, V.R., Zanetti, S.M. and Longo, E., Mater. Res., Vol. 2, 93-97 (1999).