PHOTOCATALYTIC DECOMPOSITION OF 4-CHLOROPHENOL ON MODIFIED ANATASE TiO_2: PREPARATION AND MICROSTRUCTURE OF BINARY METAL OXIDE NANO-MIXTURES: TiO_2/Fe_2O_3, TiO_2/ZnO AND TiO_2/ZrO_2. COMPARISON WITH PURE ANATASE.

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Photocatalytic decomposition of toxic organic compounds in presence of semiconducting material has been studied extensively during the last two decades. Is has been established that heterogeneous photocatalysis can be good alternative to removal organic pollutants from water and air. TiO_2 is known as the most important photocatalyst on account of its advantages over other materials, such as its higher activity, lower price and its chemical and photo resistance properties. One of this catalyst disadvantage is that the activity is still not high enough to be suitable for commercial application [1]. Many efforts have been made in order to enhance the TiO_2 catalyst activity; modify anatase surface adding some transition metal dopants (Zn^{2+}, Fe^{3+}, V^{4+}, Zr^{4+}, Mo^{6+}) or co-deposition of noble metal island (Pt, Pd, Au, Ag) on TiO_2 [2]. Choi at al. [3] reported systematically the promotion of 21 types of transition metal on TiO_2, and suggested a relationship between photocatalysis of modified TiO_2 with holes and electrons generated by illumination. Some authors [4-6] have published a correlation between the enhanced photoreactivity and higher surface activity resulting from the addition of metal oxide. Surface acidity was thought to reveal stronger surface hydroxyl groups, which accept holes generated by illumination and oxidation of adsorbed molecules [1]. These results suggested that hetero elements incorporated to TiO_2 create a novel binary metal oxide photocatalysts with high performance in photo-induced degradation of toxic organic compounds. In this contribution we reported the new binary metal oxide photocatalysts: TiO_2/Fe_2O_3, TiO_2/ZnO and TiO_2/ZrO_2 prepared via homogeneous precipitation of corresponding metal salt with urea in aqueous solution. The starting nanocrystalline anatase TiO_2 was prepared by hydrolysis of $TiOSO_4$ aqueous solution using urea as the precipitation agent. Appropriate amount of metal salt [Fe_2O_3, $Zn(NO_3)_2$, $ZrOSO_4$] was added to the starting solution and the stoichiometry of reaction was respected to obtain the final products. The activity of samples prepared in this way was studied. The microstructure and surface properties of photocatalysts were characterized by HRTEM (JEOL JEM 3010 operated at 300 kV, attached with CCD Gatan and EDS), SEM (Philips XL CP30) and BET/BJH (Coulter SA 3100). Kinetic of 4-chlorophenol disappearance in aqueous suspension was used as a test reaction. We have found that (Ti-Zr-1) sample, consisting in 1 % Zr^{4+}, exhibited the best photocatalytic efficiency of 4-CP degradation in all binary metal oxides nano-mixtures and pure TiO_2 tested. Probably, well crystallized small particles with different crystal structure and a grain size average less than 10 nm, have generated a considerable interest due to improvement obtained in several properties expected to result from nanometer scale grain-size reduction. Binary metal oxide particles (sample TiO_2/ZrO_4) at final stage of growth are approximately spherical in shape and showed a significant surface area (484 g/m^2). Pore size distribution measurement reveals that this total surface area is attributed mainly to micropores with mean pore radius under 3 nm. The average size of crystallites was calculated using Sherrer equation. Estimation shows that the mean crystal size of the individual particles was 6.1 nm and is in line with HRTEM observations (Fig. 1).

References

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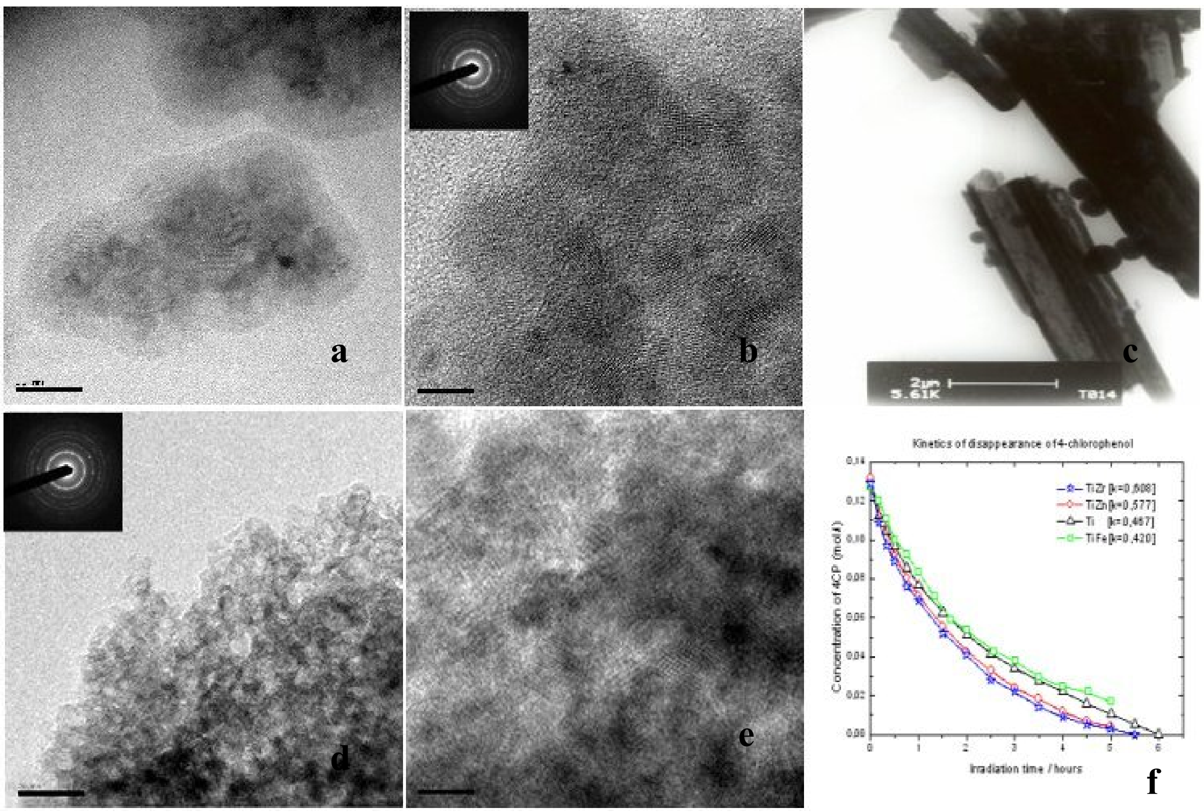

Fig. 1. (a)TEM image of TiO_2/ZnO mixture, (b) HRTEM image and ED (inset) of TiO_2/ZnO, (c) TEM image of TiO_2/Fe_2O_3, (d) TEM image and ED (inset) of TiO_2/ZrO_2 mixture, (e) HRTEM image of TiO_2/ZrO_2 mixture (f) Photocatalytic decomposition of 4-CP in the presence of TiO_2/ZnO, TiO_2/ZrO_2 and TiO_2/Fe_2O_3 nano-mixtures and pure anatase TiO_2