Photocatalysis with Fe/Ti-Pillared Clays for the Oxofunctionalization of Alkylaromatics by O2

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Abstract : A pillared montmorillonite containing iron doped titania (Fe/Ti-PILC) has been prepared from a natural clay. This material has been characterized by X-ray diffraction, nitrogen adsorption, temperature programmed desorption of ammonia, inductively coupled plasma atomic emission spectroscopy, atomic absorption, and diffuse reflectance UV-VIS spectroscopy. The layer structure of Fe/Ti-PILC resulted to be ordered with an insertion of pillars, which caused a slight increase in the basal spacing of the clay. Its specific surface area was about three times larger than that of the parent Na-montmorillonite due principally to the creation of a remarkable microporous network. The doped material was a robust photocatalyst able to oxidize liquid alkyl aromatics to the corresponding carbonylic derivatives, using O2 as the oxidizing species, at mild pressure and temperature conditions. Accumulation of valuable carbonylic derivatives was possible since their over-oxidation to carbon dioxide was negligible. Fe/Ti-PILC was able to discriminate between toluene and cyclohexane in favor of the aromatic compound with an efficiency that is about three times higher than that of titanium pillared clays (Ti-PILC). It is likely that the addition of iron favored the formation of new acid sites able to interact with the aromatic substrate. Iron doping caused a significant TiO2 visible light-induced activity (wavelength > 400 nm) with only minor negative effects on its performance under UV-light irradiation (wavelength > 290 nm).

Keywords : alkyl aromatics oxidation, heterogeneous photocatalysis, iron doping, pillared clays

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