Synthesis of Doped TiO_2 Metal Oxide Nanoparticles in Supercritical CO_2

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TiO_2 nanoparticles are interesting for many applications due to their photocatalytic properties. However, TiO_2 activity is reduced to the region of UV light (wavelength around 360 nm). In order to harness the abundant and safe potential of solar energy, the development of processes to enhance and shift the absorption of TiO_2 to the visible region is of the great importance. One of the ways to extend the absorbance of TiO_2 is transition metal doping in the lattice of TiO_2 [1]. In this work, supercritical CO_2 is used as reaction medium for the synthesis of doped TiO2 nanoparticles with Fe.

Keywords: doped TiO_2 nanoparticles, synthesis, supercritical CO_2.

Introduction

Titanium dioxide is a semiconductor which exhibit catalytic properties. It is widely used in environmental application as a photocatalyst for oxidation reactions of organic compounds, in alcohol thermal decomposition reactions, in photocatalytic decomposition of water for hydrogen production, in photovoltaic cells and etc [1].
Generally, the photocatalysis process over a semiconductor involves the absorption, band gap excitation, separation of the photoexcited electron/hole pairs, and redox reactions on the semiconductor surface [2].
As a photocatalyst TiO_2 can act as sensitizers for light – reduced redox processes due to their electronic structure, which is characterized by a filled valence bad and an empty conduction band. When the photon with an energy of hv exceeds the bandgap, E_g, of the semiconductor, an electron e^-, is promoted from the valence band, VB, into the conduction band, CB, leaving a hole h_{vb} behind. Graphically it can be expressed in Fig.1 [3].
TiO_2 (anatase) has wide band gap, $E_g \approx 3{,}2$eV, thus only light below 400 nm is absorbed and capable of forming the e^-/h^+ pair [4]. The dyes, impurities and dopants can sensitize TiO_2 to react to a much larger visible light region [1]. The different dopants may not have the same effect on trapping electrons or holes on the surface during the interface charge transfer because of the different positions of the dopant in the host lattice. In general photocatalytic activity of TiO_2 depends of many factors, such as, specific surface area, the absorption affinity and capacity for organic contaminants, electron-hole recombination processes in the bulk and on the surface of the catalyst, intensity and spectral distribution of the illuminating light, crystal morphology, intrinsic solid stated defects, stoichiometry of the catalyst oxide, pH, the presence of electron acceptors, the concentration of the pollutant [4].
The main aim of the research was focused on the efforts to synthesise doped TiO_2 nanoparticles with Fe atoms in order to change catalytic properties of TiO_2 nanoparticles which were tested in the methyl orange oxidation reactions.

Experimental

In the experimental procedure, diisopropoxititanium bis(acetylacetonate), (DIPBAT), is used as titania precursor and Iron (III) acetylacetonate and $Pd(hfa)_2$ for the doping metal ion. Under the supercritical conditions metal oxide particles are formed as a result of the

metal salt hydrolysis and followed dehydration reaction under the supercritical conditions. The great advantage of this technology is that the nanoparticle doping takes place during the synthesis process. The synthesis of doped TiO_2 nanoparticles in batch and continuous flow reactors are presented. The wide range reactions at temperature (200 – 400 °C) and pressure (200 -250 bar) have been tested. Photocatalytic activities for the degradation of methyl orange under visible light irradiation are tested for the doped TiO_2 and they are compared to the non-doped samples.

Results

The experimental results showed that TiO_2 particles with high (5%) or low Fe content (1%) can be synthesised from DIPBAT precursor using two different alcohols (isopropanol and ethanol) as the co-solvents and reactants. The addition of Fe in to the titanium precursor allows TiO_2 –Fe particles to be synthesized with the improved photocatalytic activity using visible light compared to TiO_2. The particles with lower content of Fe (1 %) exhibit more efficient photocatalytic effect that those obtained with higher content of Fe (5 %).

References

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