



# Clinoptilolite supported rutile TiO<sub>2</sub> composites: Synthesis, characterization, and photocatalytic activity on the degradation of terephthalic acid



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## ABSTRACT

Clinoptilolite supported rutile TiO<sub>2</sub> composites were synthesized for the enhancement of its photocatalytic performance in the degradation of the aqueous terephthalic acid solution under UVC illumination by the increase in its surface area and to simplify its recovery from the treated solution after use. The XRD spectra of the composites revealed the formation of pure rutile TiO<sub>2</sub> on the surface of the clinoptilolite. The SEM images showed the formation of the spherical TiO<sub>2</sub> clusters were composed of nano fibers on the surface of the clinoptilolite. For all composites synthesized, the dispersion of the TiO<sub>2</sub> particles on the clinoptilolite led to a surface area larger than that of the bare TiO<sub>2</sub> and clinoptilolite. The materials synthesized in the present study exhibited higher catalytic activity compared with the commercial Degussa P25 and anatase. Among the catalysts synthesized the TiO<sub>2</sub>/clinoptilolite with a weight ratio of 0.5 was found to be the most photoactive catalyst even though it contains a lesser amount of active TiO<sub>2</sub>. The kinetic of the reactions for different catalyst was found to be consistent with the pseudo-first order kinetic model. The results of the Langmuir-Hinshelwood model showed the slight contribution of the adsorption on the degradation. The activity of the TiO<sub>2</sub>/clinoptilolite with a weight ratio of 0.5 decreased after repetitive use due to the accumulation of the TPA molecules on the surface of the catalyst.

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## 1. Introduction

The rapid growth in technology causes environmental problems both in the air and water. In order to overcome these issues, increased effort has been carried out to improve effective and inexpensive technologies. Heterogeneous photocatalytic degradation becomes a promising technology for the treatment of water because it is cheap and environmentally friendly. In this method, semiconductors are used as the photocatalyst and solar light as the energy, and the degradation reaction can be carried out under ambient conditions. The TiO<sub>2</sub> nano particles are one of the most preferred photocatalyst due to their low toxicity, chemical inertness, photostability, and high photocatalytic activity for the degradation of various organic compounds [1–3]. The crystal structure, size, shape, surface, and optical characteristic of the TiO<sub>2</sub> particles are crucial properties that affect their performances in photocatalytic degradation. Therefore, the studies regarding the synthesis of photoactive TiO<sub>2</sub> has gained interest in recent years. The main

crystal structures of TiO<sub>2</sub>, anatase, rutile, and brookite, show specific physical, chemical, and optical properties. Although TiO<sub>2</sub> nano particles exhibit high photocatalytic activity in the degradation reactions, recovery problems from the treated solution for reuse limits its application on an industrial scale. In order to improve their recovery from the treated solution they are dispersed on different kinds of supports having high adsorption capacity. The dispersion of TiO<sub>2</sub> on a support provides high specific surface area which enhances the degradation performance. The materials used as a support for TiO<sub>2</sub> particles are generally SiO<sub>2</sub> [4–9], activated carbon [10,11], and zeolites [2,3,12–15]. Among these supports, zeolites have attracted interest due to their unique structures, uniform pores, and channels [16–18]. Zeolites can be synthesized using different methods or obtained from natural sources. Although the properties of the synthetic zeolites can be easily tuned during the synthesis, natural zeolites are cheap, easily available, and abundant but require some chemical treatments to obtain a clean surface.

The TiO<sub>2</sub>/zeolite composites are generally synthesized by the sol-gel, solvothermal and hydrothermal methods using organic and inorganic titanium precursors. Most of the composite synthe-

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sis covers calcination at high temperatures (200–800 °C) to improve the crystal structure [2,3,13–17,19]. Since anatase is generally accepted as the most photoactive TiO<sub>2</sub>, the studies generally focused on the calcination temperature for the formation of the anatase phase on a support [2]. However, due to the superior properties of rutile, that are thermodynamically stable and possess chemical inertness even in acidic and basic conditions, in recent years, the attraction to synthesize rutile TiO<sub>2</sub> has increased [1,20–24]. The synthesis of rutile TiO<sub>2</sub> generally consists of calcination at high temperatures for the transformation of the amorphous or anatase structures to rutile which increases the energy requirement and agglomeration of the particles. Therefore, the development of the methods and specifying the conditions for the synthesis of rutile TiO<sub>2</sub> with controlled properties at moderate conditions is important.

The studies regarding the synthesis of TiO<sub>2</sub> particles on clinoptilolite which is a natural zeolite generally consist of anatase TiO<sub>2</sub> particles obtained using TiCl<sub>4</sub> or TTIP as Ti precursor and calcination at high temperatures for phase change [3,14–17,19,25]. Trujillo et al. [14] studied the synthesis of anatase TiO<sub>2</sub>/clinoptilolite composites using TiCl<sub>4</sub> as the titanium precursor with a final step of calcination at 400 °C and used them as a catalyst in the photocatalytic degradation of anionic and cationic contaminants. Wang et al. [15] synthesized clinoptilolite supported Cr-doped TiO<sub>2</sub> photocatalyst with a TiCl<sub>4</sub> precursor for the degradation of methyl orange under UVC illumination. They investigated the effects of the ion concentration and calcination temperature on the structure and photocatalytic activity of the composites. Petkowicz et al. [19] used zeolite NaA, synthesized using different silicon sources, as the support for the TiO<sub>2</sub> produced by TiCl<sub>4</sub> followed by calcination. Their photocatalytic activities were investigated in the degradation of methylene blue under UVA irradiation.

In the present study, the rutile TiO<sub>2</sub>/clinoptilolite composites were synthesized by the hydrolysis of TiCl<sub>4</sub> on a clinoptilolite support at 95 °C and their photocatalytic activities were examined in the degradation of terephthalic acid (TPA) which is a raw material produced in millions of tones all over the world for the manufacture of polyester fibers and films [26]. The wastewater containing TPA may cause serious problems such as acute, chronic, and molecular toxicity to organisms [27,28]. The novelty of the present study is the synthesis of rutile TiO<sub>2</sub> particles on clinoptilolite at moderate temperature without calcination and their usage as catalyst in the degradation of TPA under UVC illumination which was not reported in literature before. The method and conditions in the present study provide a simple, one-step, and moderate temperature technique by which rutile TiO<sub>2</sub> particles can be synthesized with the desired properties without calcination.

## 2. Experimental

### 2.1. Materials

Titanium tetrachloride (TiCl<sub>4</sub>, >99% purity, Merck) was used as a titanium precursor and hydrochloric acid (HCl, 38 wt%, Merck) as a solvent. Natural zeolite tuff (Gördes-Turkey) kindly supplied by INCAL MINERAL Co. was used as the support. Commercial Degussa P25 (30% rutile and 70% anatase), Rutile (Kronos) and Anatase (Sigma) were used as TiO<sub>2</sub> references. Terephthalic acid (TPA), with a high purity (>99.6%) was kindly supplied by PETKİM Petrochemical Co. and was selected as the model organic pollutant. All chemicals were used as received without further purification. The conductivity and pH of the double distilled water used in the study was 1.3 μS cm<sup>-1</sup> and 6, respectively.

### 2.2. Preparation of the support

Natural zeolite tuff with a particle size of 5 cm was ground in a jaw crusher (Fritsch GmbH) and then wet sieved to ≤38 μm. The tuff was purified using distilled water and HCl solution as given detailed in a previous study [29]. The elemental content of the natural zeolite was analyzed with an atomic absorption spectrophotometer (AAS, Varian SpectraAA-10Plus) and found that SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and CaO in weight percentages of 75.5, 14.6, 5, and 3%, respectively, are the main components of the zeolite and the remaining contains trace amounts of other oxides such as Fe<sub>2</sub>O<sub>3</sub>, MgO, MnO, TiO<sub>2</sub>, and Na<sub>2</sub>O. Considering the Si/Al mole ratio (Si/Al = 4.38 > 4) [30] and the ratio of the sum of the divalent cations to the sum of the monovalent cations changing between 0.5 and 0.8 ( $\sum M^{++} / \sum M^+ = 0.58$ ) [31], the tuff is defined as clinoptilolite.

### 2.3. Synthesis of TiO<sub>2</sub> on clinoptilolite support

The TiO<sub>2</sub>/clinoptilolite composites were synthesized by the acid hydrolysis of TiCl<sub>4</sub> on the clinoptilolite. The procedure reported by Yener and Helvacı [4,32] was followed for synthesis. Briefly, the aqueous solution of TiCl<sub>4</sub> (0.5 M) was prepared using HCl (3 M) to control the fast hydrolysis reaction of the TiCl<sub>4</sub> in water. In a typical synthesis, 250 mL of acidic TiCl<sub>4</sub> solution was added to the 20 and 10 g clinoptilolite for TiO<sub>2</sub>/clinoptilolite weight ratios of 0.5 and 1, respectively, in a home-made reactor system. The hydrolysis reaction was carried out at 95 °C for 3 h, at a constant stirring rate of 500 rpm under reflux. After aging at room temperature for 24 h, the white precipitate and yellow supernatant were separated to analyze with AAS. The existence of Ti in the supernatant was evaluated as the unconsumed reactant of TiCl<sub>4</sub> and used for the calculation of the reaction efficiency. The other ions detected by AAS were the elements dissolved from the zeolite tuff due to the acidic reactant solution and resulted in a yellow supernatant. The precipitate was repeatedly washed with water to decrease the acidity of the suspension by removing the Cl ions until the pH of the rinsing water became neutral and then dried at 60 °C for 1 day. The composites synthesized at TiO<sub>2</sub>/clinoptilolite weight ratios of 0.5 and 1 were denoted as TZ05 and TZ, respectively. Their photocatalytic activities were compared with those of the clinoptilolite and TiO<sub>2</sub> nano particles labeled as Z and T, respectively. The TiO<sub>2</sub> particles were synthesized using the same procedure without zeolite support under the same reaction conditions.

### 2.4. Characterizations

The quantitative analyses of the elements in the clinoptilolite and in the supernatant separated at the end of the composite synthesis were performed with X-ray fluorescence (XRF, Spectro IQ II) and an AAS analysis. The crystal structure of the particles was identified by X-ray diffraction (XRD, Philips X'pert PRO – 45 kV, 40 mA) with a 2θ ranging from 5 to 75° using Cu Kα radiation. The crystallite size of the particles was calculated using the Scherrer equation,  $D = K\lambda / \beta \cos \theta$ , where  $D$  is the crystallite size (nm),  $K$  is the crystallite-shape factor of 0.9,  $\lambda$  is the X-ray wavelength which is 0.15418 nm for CuKα,  $\beta$  is the X-ray diffraction broadening measured at half the line maximum intensity (radian), and  $\theta$  is the diffraction angle (°) observed. The chemical structures of the products were specified by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum 100, Diamond/ZnSe crystals). The samples together with KBr (Sample: KBR = 1: 100 by weight) were pressed into pellets, and their analyses were performed at a resolution of 4 cm<sup>-1</sup> over the 4000–600 cm<sup>-1</sup> region in the transmittance mode. The specific surface areas and pore sizes of the samples were determined by means of N<sub>2</sub>

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