



Gas-phase Photocatalytic Mineralization of n-Hexane over N-doped TiO₂ Nanoparticles under Visible-Light

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INTRODUCTION

Among all the air pollutants, volatile organic compounds (VOCs) have attracted considerable attention in the past decades [1]. All carbon-based organic chemicals present in atmosphere have been termed as VOCs, excluding elemental carbon, carbon monoxide, and carbon dioxide. Among wide variety of volatile organic compounds like alkanes, alkenes, alcohols, aldehydes, ketones, aromatics, many of them have been known as toxic and carcinogenic, mutagenic, or teratogenic agents [2].

In recent years, gas-phase photocatalytic oxidation (PCO) is the way for destruction of VOCs and declining environmental pollutants, which can mineralize many organic materials into odorless and non-malignant compounds, i.e. CO₂ and H₂O, at near ambient temperatures with atmospheric oxygen as oxidant agent, and using nano-semiconductor catalysts and ultraviolet

(UV) light [1,3].

Several kinds of oxide and sulfide semiconductors having adequate band gap energies have been examined for catalyzing a wide range of chemical reactions. TiO₂ in spite of its high photocatalytic activity, non-toxicity, photochemical stability, and low cost cannot be photoexcited by visible-light of free solar radiation due to its wide band gap energy [4]. One effective approach for overcoming to practical drawback of TiO₂ is doping photocatalyst with transition metal or non-metal impurities. Insertion of C, F, S, and N as most current non-metal dopants resulted in the development of visible-light active titania photocatalysts mostly via narrowing the band gap of TiO₂ [5]. Nitrogen, owing to its small ionization energy, comparable atomic size with oxygen, and high stability can be smoothly incorporated into the TiO₂, as substitutional element on the oxygen of lattice or at interstitial lattice sites [6]. In the

current study, the photocatalytic mineralization of n-Hexane using N-doped TiO_2 nanoparticles coated on stainless steel mesh under visible-light irradiation was investigated.

EXPERIMENTAL PROCEDURE

CATALYST PREPARATION

The procedure applied to coat TiO_2 on the supports is described in literatures [3]. The webnets were immersed and rotated in the slurry of TiO_2 and followed by drying at temperature room, putting in an oven at 120 °C, and calcinating in 350 °C. Also, N-doped TiO_2 photocatalyst was prepared by immersing the calcinated titania webnet in guanidine carbonate aqueous solution in a total dark space. In addition, drying and calcination processes of the sample were similar to what mentioned above.

CATALYTIC ACTIVITY TEST

The activity of the prepared catalysts was evaluated by photocatalytic degradation of n-Hexane in a 1000 mL self-designed photocatalytic batch reactor made of stainless steel, under UV and visible irradiation. A 125 W high pressure mercury lamp was set in the center of the reactor to prepare direct UV illumination on the catalyst surface. Also, a glass bulb with a special coating could prepare visible-light via filtering UV. Also, the sealed reactor was vacuumed and occupied with extreme pure mixture of O_2 and He with a ratio of O_2 : He=2:1 at gauge pressure up to 3 bar and the temperature of 65 °C. The gaseous mixture was sampled once every 30 min to analyze the conversion efficiency of n-Hexane by GC and FTIR analyses.

RESULTS AND DISCUSSION

CHARACTERIZATION RESULTS

Fig. 1 illustrates the XRD patterns of TiO_2 and

N-doped TiO_2 samples. In addition, the average crystal sizes of the samples according to the Scherrer's equation, and anatase phase content are listed in Table 1. It must be emphasized that the crystal size has a strong effect on photoactivity. These results are consistency with consequences from XRF analysis recorded in Table 2. This analysis was applied to identify the weight fraction composition of samples.

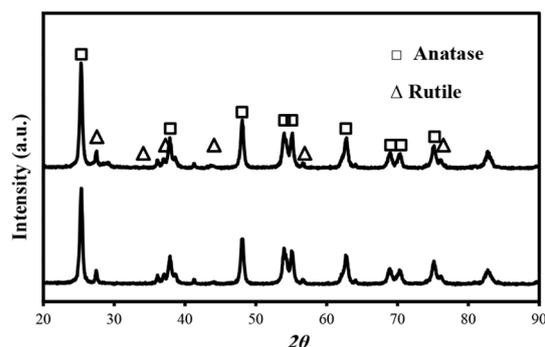


Figure 1: XRD patterns of TiO_2 and N-doped TiO_2 .

Table 1: Physical properties of photocatalysts.

Photocatalyst	Ave. crystal size (nm)	Anatase (%)
TiO_2 (P25)	19.1	85.6
N- TiO_2	16.0	84.2

Table 2: XRF analysis of prepared photocatalysts.

Comp. (%)	Photocatalyst	
	TiO_2	N-doped- TiO_2
TiO_2	97.31	96.11
N	0.002	0.83

The morphological changes in the surface of two TiO_2 samples through SEM micrographs are shown in Fig. 2. As can be seen, the mesh surface in all of the samples were coated uniformly by TiO_2 nanoparticles, and nitrogen doping led to more roughness and some small observable pores in the catalyst surface. Also, the FTIR spectra of two TiO_2 photocatalysts are shown in Fig. 3. The FTIR spectra at 900-3900 cm^{-1} is in accordance with some previous records.

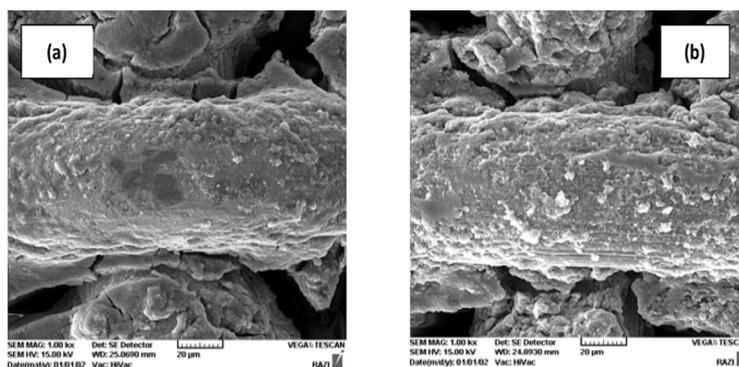


Figure 2: SEM images of the coated stainless steel webnet supports with, (a) TiO_2 and (b) N-doped TiO_2 .

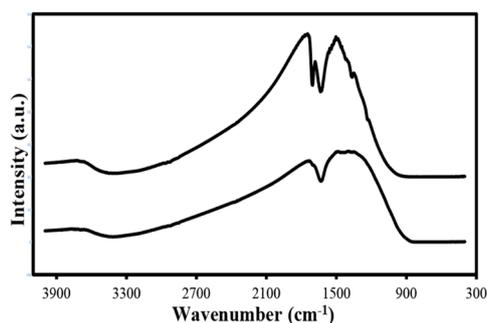


Figure 3: FTIR spectra of photocatalyst samples.

PHOTOCATALYTIC ACTIVITY

The photocatalytic activity of N- TiO_2 under visible-light was examined through photocatalytic conversion of gaseous n-Hexane into CO_2 and H_2O (Fig. 4). According to the curves, an almost complete photoconversion with the same trends was obtained during the time of experiments. Also, by decreasing the initial concentration of n-Hexane from 40 to 20 and 10 g/m^3 , the concentration of photogenerated products decreased from 120 to 30 g/m^3 , respectively.

CHARACTERIZATION OF PRODUCTS

Intensity of CO_2 peaks in the various FTIR curves of the Fig. 5 indicates that the N-modified catalyst is the most efficient ones for degradation of n-Hexane and production of CO_2 .

MECHANISM ASPECTS

In general, photocatalytic oxidation of alkanes leads to formation of intermediates such as aldehydes and ketones, and CO_2 and H_2O are the final products. Also, the final product from the chain PCO reactions of alkanes can be finally derived from photodecarboxylation reaction of carboxylic acids in the presence of TiO_2 .

CONCLUSIONS

The photocatalytic conversion about 93% was obtained by the N-doped TiO_2 /Visible-light. As the major consequence, the mineralization efficiency of n-Hexane by N-doped TiO_2 /visible-light was higher than that of TiO_2 /UV. In addition, a good mineralization ca. 100% was obtained by 10 g/m^3 initial n-Hexane concentration during 2 h using N-doped TiO_2 under visible-light.

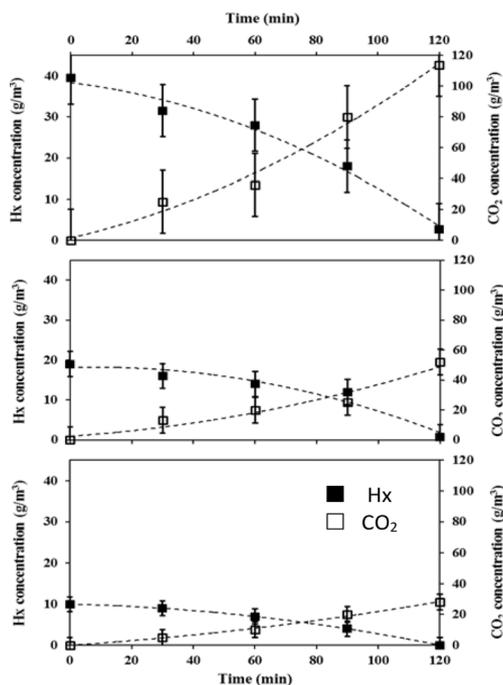


Figure 4: The photocatalytic conversion of n-Hexane over N-doped TiO_2 sample under visible-light illumination by varied n-Hexane (Hx) concentrations.

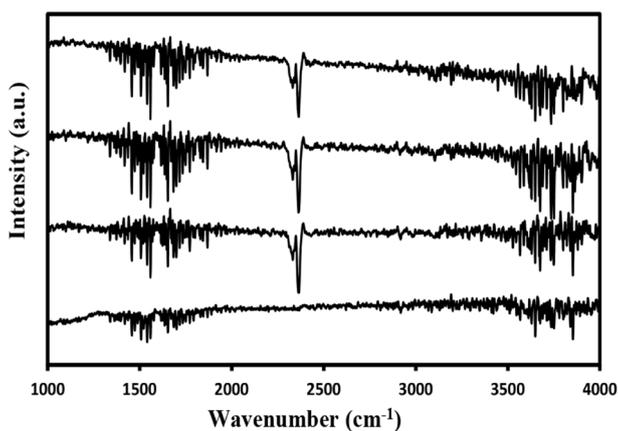


Figure 5: FTIR spectra of products under different photocatalytic conditions.

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