RESEARCH PAPER

Nano Sized Ni/TiO_2 @ NaX Zeolite with Enhanced Photocatalytic Activity

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ABSTRACT

Nickel doped TiO_2 nano particles (1% w/w) were prepared and immobilized on NaX zeolite and after characterization by X-ray diffraction and scanning electron microscopy used as photo catalyts for degradation of orange G. The X-ray diffraction patterns show that the supported TiO_2 are crystallized in anatase form and the intensity of the zeolite peaks decreases with the increase of TiO_2 loading. Scanning electron micrographs of synthesized samples show that nano size titanium dioxide particles are accumulated on the surface of the zeolite. These materials are applied as photo catalysts for the degradation of orange G in aqueous solution by means of ultraviolet light irradiation at room temperature. The effect of solution pH, ultraviolet irradiation time and catalyst in degradation of orange G was investigated. The results show that nickel doped TiO_2/NaX zeolite as a photo catalyst in degradation of orange G in acidic solution is superior to the Ni/TiO_2 nano composite and also undoped nano size titanium dioxide particles.

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INTRODUCTION

In recent years semiconductor photo catalyst has been used as an efficient technology to overcome environmental problems [1-3]. Among various semiconductors TiO_2 in anatase form has been mostly studied because of its photo catalytic activity for mineralization of organic pollutants into carbon dioxide and water under UV irradiation. But this technology only works under ultraviolet light because of TiO_2 large band gap [4-6]. Solar light contains only 4% ultraviolet light when it reached to earth surface. So modification of TiO_2 is necessary to enhance the efficiency of its photo catalytic activity [7-9]. Among different approaches for modifications of TiO_2, using supported titanium dioxide has allowed to enhance the photo degradation rates significantly [10-15]. Also doping TiO_2 with metal ions may improve its photo activity [15-22]. To our knowledge nickel doped TiO_2 nano particles has not be applied for the photo degradation of Orange G (OG) aqueous solutions.

In this work, the photo catalytic degradation of Orange G (OG) aqueous solutions was investigated using nano sized anatase titania prepared by sol-gel method. To improve the photo catalytic efficiency, nickel doped TiO_2 nano particles were synthesized and immobilized on NaX zeolite and used as a novel photo catalyst for the degradation of Orange G under UV irradiation. Also the dependency of degradation yield on various parameters such as the pH of the photo degradation reaction, time of UV irradiation and the weight ratio of Ti/Si have been investigated.

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MATERIALS AND METHODS

Chemicals

Analytical grade nitric acid, sodium hydroxide, isopropanol, nickel nitrate hexahydrate, Orange G (OG) dye ($C_{16}H_{10}N_2Na_2O_7$) and tetraisopropyl orthotitanate, as a titania source, were purchased from Merck and used without further purification. NaX zeolite was obtained from SPNI Corporation, Iran and deionized water was used in all experiments.

Synthesis of Ni doped TiO_2/ NaX zeolite photocatalyst

Stable TiO_2 sol was synthesized by acid hydrolysis of tetraisopropyl orthotitanate [23]. Ni doped TiO_2 were prepared by adding Ni $(NO_3)_2.6H_2O$ solution to a stable sol of TiO_2 (1/99 weight ratio of Ni/Ti, respectively) Then the slurry was dried at 313 K and calcined at 673 K for 3 h. In a typical preparation of supported photo catalyst, 4.0 g of zeolite was suspended in 100 mL of water and then mixed with 0.144 g of Ni/TiO_2 sol (weight ratio of Ti/Si = 20%) while stirring for 24 h. Finally the mixture was dried at 343 K and calcined at 673K for 3 h.

Photo catalytic activity tests

In separate experiments, 50 mL of Orange G aqueous solutions with the initial concentrations of 10 ppm were mixed with 0.3 g of catalyst at pH 5, 7 and 9 for all three photo catalysts (TiO_2, Ag/TiO_2 and Ni/TiO_2/NaX zeolite). Prior to irradiation the suspensions were stirred for 30 min in dark and then irradiated for various duration of time. All degradation experiments were performed in a batch quartz photo reactor under a 125 W mercury lamp (λ_{max}=254 nm) as ultraviolet light source. Finally at the predetermined time intervals, 2 mL aliquots were withdraw from the reactor, centrifuged to remove the catalyst and analyzed for the photo degradation of Orange G by UV–vis spectrophotometer (SHIMADZU-2550). Photo catalytic degradation processes were carried out with nano crystalline TiO_2, Ni/TiO_2 and NiTiO_2/NaX zeolite, in different pH values and in separate batches. All photo catalyst preparation and photo degradation measurements were repeated at least three times to confirm reproducibility. Phase analysis of the samples was carried out by X-ray diffraction (XRD; D4-BRUKER diffractometer by Cu Kα radiation at 20KV and 30mA). Morphology of photo catalysts was observed by a Philips XL-30 scanning electron microscope.

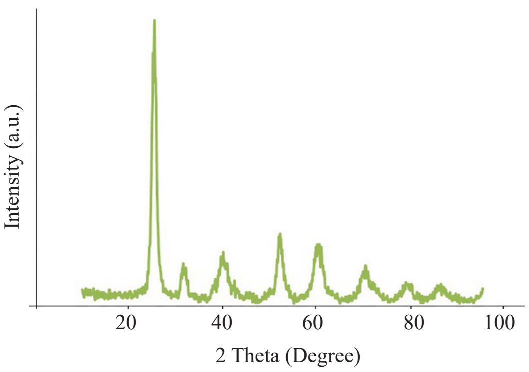

Fig. 1. XRD pattern of Ni/TiO_2 nano-composite.

RESULTS AND DISCUSSION

Catalyst characterization

The XRD pattern of Ni doped TiO_2 nano particles that calcined at 673K for 3 h is shown in Fig. 1. It shows five clear diffraction peaks at 25.48, 38.24, 48.12, 54.96, 63.48, 70.75 and 74.99°. This pattern shows that prepared powder is well crystallized in TiO_2 anatase phase (International Centre for Diffraction Data card File No. 21-1272). Due to the very small dopant contents (1%), no obvious diffraction line for Ni is observed. Fig. 2 shows the XRD patterns of the supported photo catalysts, where the appearance of a diffraction peak at 2θ = 25.48° is characteristic of anatase phase of titanium oxide and this reflection (101) increases with increasing of titania loading on zeolite. The average particle size of Ni/TiO_2 was calculated by applying the Scherrer's formula on the anatase diffraction peak (101) which is shown in Fig. 1 (2θ = 25.4°) and is estimated by10 nm [24].

Fig. 3 shows the micrographs of zeolite NaX and Ni/TiO_2/NaX zeolite (with weight ratio of Ti/Si=20%) samples. The images show that the clean surface of zeolite crystals is covered by the Ni/TiO_2 species and there is no change in the typical morphology of zeolite after loading of Ni/TiO_2.

Photo catalytic decomposition of Orange G (OG)

The pH has a pronounce effect on the photo degradation efficiency of organic pollutants [25]. TiO_2 is reported to have higher oxidizing activity at lower pH but the NaX zeolite is not stable in pH less than 3. As shown in Fig. 4, TiO_2, Ni/TiO_2 and Ni/TiO_2/NaX zeolite, as catalysts in photo degradation of orange G, are more effective in acidic conditions. Therefore, the photo degradation of orange G solutions were carried out in pH = 5.

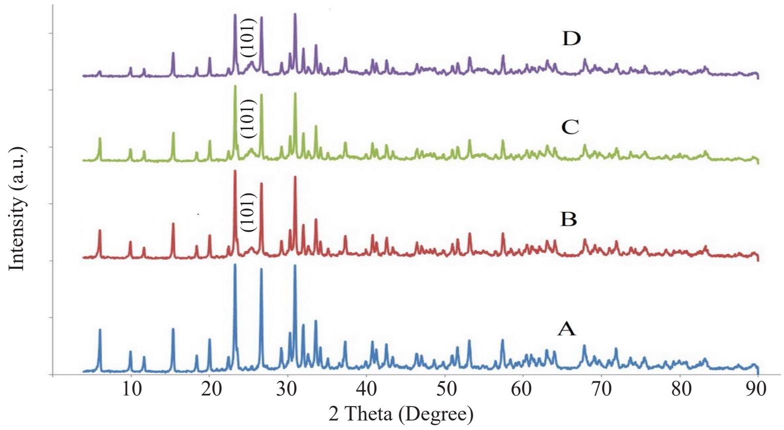

Fig. 2. XRD patterns of NaX zeolite (A), Ni/TiO_2/NaX zeolite with weight ratio of Ti/Si=10% (B), 20% (C) and 30% (D).

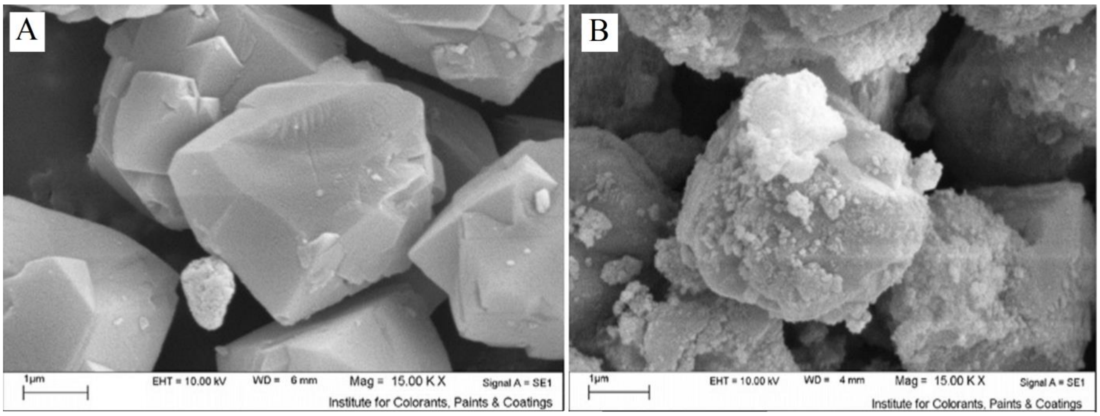

Fig. 3. SEM images of NaX zeolite (A), Ni/TiO_2/NaX zeolite with weight ratio of Ti/Si= 20% (B).

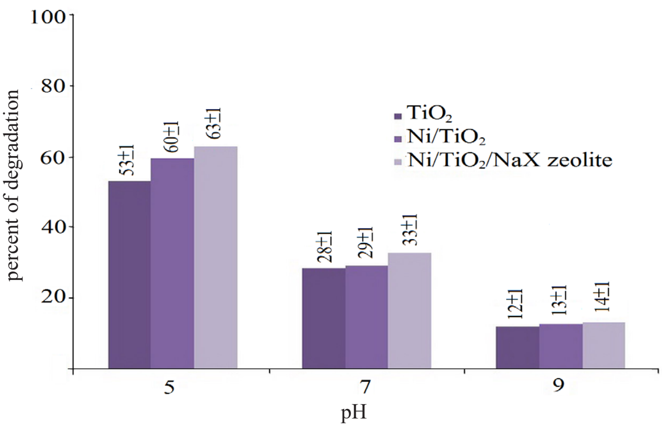

Fig.4. Degradation percentage of orange G using synthesized TiO_2, Ni/TiO_2 and Ni/TiO_2/NaX zeolite with weight ratio of Ti/Si=20% catalysts under 90 min UV irradiation at various pH values at room temperature.

The effect of irradiation time on the photo catalytic degradation of orange G in the presence of synthesized TiO_2, Ni/TiO_2 and Ni/TiO_2/NaX zeolite are shown in Fig. 5. After 150 min irradiation, the degradation yields of orange G by utilizing synthesized TiO_2, Ni/TiO_2 and Ni/TiO_2/NaX zeolite (with weight ratio of Ti/Si=20%) reached to 81.87%, 87.21% and 92.1%, respectively.

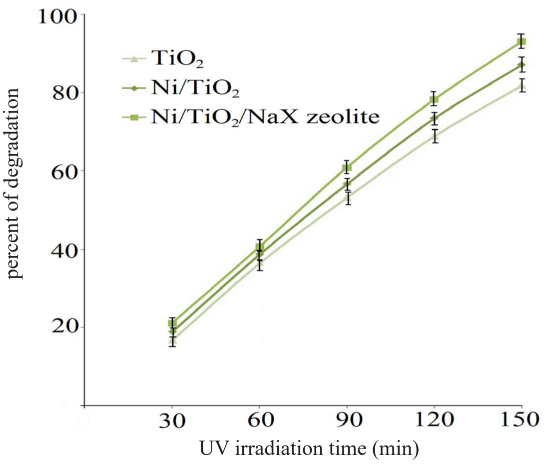

Fig. 5. Degradation percentage of orange G using synthesized TiO_2, Ni/TiO_2 and Ni/TiO_2/NaX zeolite with weight ratio of Ti/Si=20% catalysts under different times of UV irradiation at room temperature (pH=5).

CONCLUSIONS

- Ni/TiO_2 nano composite based on NaX zeolite is very effective for the photo catalytic decomposition of orange G which is a textile waste water pollutant.
- It was observed that the optimum pH value and UV irradiation time for Ni/TiO_2/NaX zeolite photo catalyst are 5 and 150 min, respectively.
- The TiO_2 sample when doped with nickel ions enhances its photo catalytic activity for the degradation of OG dye solutions up to 6.5%. Furthermore, supporting Ni/TiO_2 on NaX zeolite improves its photo catalytic efficiency up to 5.7%.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publicaton of this manuscript.

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