



Synthesis and characterization of a novel tungstosilicic acid immobilized on zeolites catalyst for the photodegradation of methyl orange



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ABSTRACT

Materials based on tungstosilicic acid (TSA) immobilized on zeolites (NH₄Y and NH₄ZSM5) were prepared by wet impregnation of the zeolite matrix with TSA aqueous solutions. The concentration was varied in order to obtain TSA contents of 5%, 10%, 20%, and 30% w/w in the solid. Catalysts were further characterized by N₂ adsorption–desorption isotherms, FT-IR, XRD, DRS-UV–vis and SEM techniques. The resulting materials were evaluated in the photodecomposition of azo dye methyl orange. The results revealed that the materials present suitable properties to be used as catalysts in the photocatalytic treatment of wastewater containing dyes, and the photodegradation follows a pseudo-first-order kinetics. Reaction parameters such as TSA content, catalysts mass, reuses and pH, were evaluated.

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1. Introduction

Wastewaters resulting from human activities can contain many organic and inorganic substances and they are one of the main sources of environmental pollution due to the fast industrial development. Anthraquinone, arylmethane, indigoid and azo dyes, used on a large scale particularly in textile industries, may generate toxic substances through oxidation, hydrolysis or other chemical reactions occurring in the wastewater phase [1]. For this reason, the development of procedures to control or destroy this type of pollution is of great interest and a challenge.

Up to the present time, different methods have been developed for removing colored pollutants from wastewaters. The most common methods are coagulation/flocculation and removal by activated carbon [2–4] which generates huge amounts of sludge

and waste that should be disposed. A new and effective approach for the removal and degradation of dyes are the advanced oxidation processes (AOPs). Among the different AOPs, the photoassisted catalytic decomposition of organic pollutants employing semiconductors as photocatalysts is promising [5,6].

Methyl orange is an azo dye that has been widely used as a model compound for the research on photoreactions [7,8]. Many researchers have reported the decomposition of methyl orange using TiO₂ as a photocatalyst under ultraviolet irradiation or solar irradiation [9–12].

Heteropolyacids with Keggin structure have received increasing attention in many research applications, such as acid catalysts and redox [13–15]. Currently, heteropolyacids are used as photocatalysts for the degradation of organic pollutants in water due to their nontoxicity and photostability [16–18]. Tungstophosphoric acid (H₃PW₁₂O₄₀, TPA) is one of the most studied and used heteropolyacids due to its high Brønsted acidity, high thermal stability and low reducibility, among other qualities [19–21]; tungstosilicic acid (H₄SiW₁₂O₄₀, TSA) shows similar and comparable characteristics, but is less taken into account.

Heteropolyacids have photocatalytic properties comparable to the best-known semiconductors such as TiO₂, ZnO, CdS, etc. [22,23].

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Both TPA and TSA absorb in the region of visible and near UV, generating a charge-transfer excited state of the isolated metal oxospecies $[\text{Me}^{(n-1)+}\text{-O}^*]$ formed. The difference between TPA and TSA lies primarily in the charge difference in the heteropolyanion. Choi et al. [24] evaluated the redox behavior and catalytic properties of Keggin-type heteropolyacids (Co^{2+} , B^{3+} , Si^{4+} and P^{5+}) in the oxidation of benzaldehyde and determined the potential reduction, which was correlated with the heteropolyanion charge. It was also reported that the charge difference generates different interactions between the heteropolyacids and the solid surfaces. Pruthiarenun et al. [25] synthesized and compared brookite hybrid films with TPA and TSA, demonstrating that the higher charge of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ with respect to $[\text{PW}_{12}\text{O}_{40}]^{3-}$ results in lower interaction with the material.

The main drawback of polyoxometalates as catalysts is their low surface area (lower than $10\text{ m}^2/\text{g}$) and high solubility in polar organic solvents and water, which makes it impossible to recover and reuse these materials [26,27]. Such problem could be overcome by supporting them on suitable porous materials with high surface area to obtain a greater number of available and accessible acidic sites. The high surface area could result in a high concentration of active catalytic sites. Moreover, the supported heteropolyacids are more thermally stable than ion exchange resins and they are practically insoluble [28]. It was reported that polyoxometalate salts were combined and supported on photoactive and/or inactive materials seeking to improve their properties [29–31]. Supporting the polyoxometalates on solid surfaces, such as zeolites, activated carbon, SiO_2 , Al_2O_3 , among others [32], increases their specific surface area and allows an easy recovery and reuse of hybrid catalysts.

Zeolites are microporous crystalline aluminosilicates with structural characteristics, such as the ability to trigger photoinduced electron donor and acceptor reactions, which makes them attractive hosts for photochemical applications [33,34]. The application of zeolites as supports provides photospecific properties such as the control of charge-transfer and electron-transfer processes, causing an increase in the photoactivity of the catalysts obtained [35,36]. This increase has been attributed, among other factors, to the stabilizing effect on the redox species photogenerated, and control over charge-transfer and electron-transfer processes [36–38]. The stabilization of the charge-transfer state of many reactions and transient species, such as $\cdot\text{OH}$ and $\cdot\text{O}^{2-}$ in the presence of zeolites, has also been reported in several studies [39–46]. Additionally, the acidity of zeolite plays a crucial role on the Keggin anion stability, because it is strongly related with the acidity of the support. For example, when NH_4Y and $\text{NH}_4\text{ZSM5}$ zeolites were used as supports for tungstophosphoric acid (TPA), the Keggin structure was more stable on ZSM-5 and it was attributed to its higher acidity [47]. When Al_2O_3 was evaluated as support for TPA, the Keggin anion was partially transformed into the $[\text{P}_2\text{W}_{21}\text{O}_{71}]^{6-}$ specie [32].

Chen et al. [48] employed HZSM5 zeolite with a Si/Al ratio of 14.2 for in situ synthesis and impregnation of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, obtaining an improvement in the *n*-octane hydroconversion. Pamin et al. [29] found that TPA was stabilized when it was supported in lower Si/Al ratio (2.47) zeolite Y. We reported [47] that both NH_4Y (Si/Al = 2.47) and $\text{NH}_4\text{ZSM-5}$ (Si/Al = 17) zeolites were suitable for TPA immobilization. Even when a huge number of ordered porous materials and amorphous silicoaluminates could be employed as supports for the heteropolyacids, zeolites were selected based on the before mentioned studies.

In the present work we attempted to combine the well-known but not deeply investigated photocatalytic properties of TSA and the above-mentioned properties of zeolites as heteropolyacid supports in order to synthesize heterogeneous photocatalytic materials. The resulting materials were evaluated in the photodecomposition of azoic dye methyl orange. We also analyzed a kinetic

study of the degradation of methyl orange employing a new material for this process (TSA-Zeolite) as heterogeneous photocatalytic materials with the objective of applying the photoreaction to water cleanup technology.

2. Experimental

2.1. Catalyst preparation

The zeolite NH_4Y (Si/Al = 2.47) was provided by Aldrich. ZSM-5 material (Si/Al = 17) was obtained by the hydrothermal crystallization method [49] with some modifications made by our group. Aqueous solution of sodium aluminate (NaAlO_2 , Johnson Matthey Electronics) was added to a silica anhydride (Fluka) solution that was previously prepared by partial dissolution of tetrapropylammonium hydroxide (TPAOH, Fluka) in water. The obtained gel reached a pH > 9 and was maintained at 120–160 °C for 12–16 days under self-generated pressure on autoclave. Afterwards, the reaction products were extracted, washed and dried at 100 °C for 12 h. The structure directing agent (TPAOH) was desorbed in N_2 atmosphere (20 ml/min) at programmed temperature (10 °C/min) from 25 to 500 °C and then it was calcined in air at 500 °C for 12 h to obtain Na-ZSM5. The ammonium form of the material ($\text{NH}_4\text{ZSM5}$) was prepared by ion exchange with NH_4Cl (1 M) for 40 h at 80 °C from Na-zeolite.

The TSA solutions were prepared from tungstosilicic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 23\text{H}_2\text{O}$, Fluka p.a.) and using distilled water as solvent. TSA was incorporated into the zeolite matrix by wet impregnation in a rotary evaporator at 80 °C. The solids were calcined in air at 200 °C for 2 h. The amount of TSA deposited onto the surface of the zeolites was varied with the purpose of obtaining a TSA concentration of 5%, 10%, 20% and 30% by weight in the final solids, named TSA05 NH_4Y , TSA10 NH_4Y , TSA20 NH_4Y , and TSA30 NH_4Y , respectively; and for zeolite $\text{NH}_4\text{ZSM5}$, TSA05 $\text{NH}_4\text{ZSM5}$, TSA10 $\text{NH}_4\text{ZSM5}$, TSA20 $\text{NH}_4\text{ZSM5}$ and TSA30 $\text{NH}_4\text{ZSM5}$, respectively.

For comparative purposes, the ammonium salt of tungstosilicic acid $[(\text{NH}_4)_4\text{SiW}_{12}\text{O}_{40}]$ was synthesized following a previously reported procedure [50]. An aqueous solution of NH_4Cl [0.073 mol/l] was added dropwise to ca. 50 ml of a 50/50 ethanol/water solution of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ [0.025 mol/l] under vigorous stirring to form a white colloidal solution, which contains well-dispersed $(\text{NH}_4)_4[\text{SiW}_{12}\text{O}_{40}]$ precipitates. The rate addition was ca. 0.4 ml/min, and the time taken for the addition of NH_4Cl was ca. 150 min. During the procedure, the $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ solution was kept at a constant temperature of 25 °C. The resulted solution was aged for 30 min at the same temperature. Then, it was dried at 55 °C with a vacuum rotary evaporator to obtain the white powder of $(\text{NH}_4)_4[\text{SiW}_{12}\text{O}_{40}]$.

2.2. Sample characterization

The specific surface area and the mean pore diameter of the solids were determined from the N_2 adsorption-desorption isotherms at the liquid-nitrogen temperature, obtained using Micromeritics PulseChemisorb 2700 equipment. The solids were previously degassed at 100 °C for 2 h.

The Fourier transform-infrared (FT-IR) spectra of the solids were obtained using a JASCO 5300 spectrometer and pellets in KBr in the 4000–4000 cm^{-1} wavenumber range.

The X-ray diffraction (XRD) patterns were recorded with Philips PW-3020 equipment with a built-in recorder, using $\text{CuK}\alpha$ radiation, nickel filter, 20 mA and 40 kV in the high voltage source, and scanning angle between 5 and 50° 2θ at a scanning rate of 2° per minute.

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