

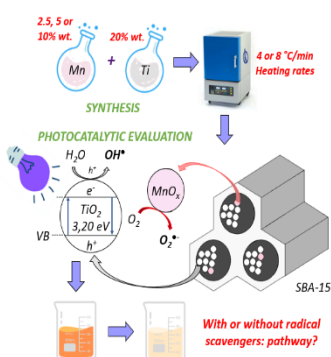
Mn and Ti-modified SBA-15 materials: a pathway for the development of radical-specific photocatalytic reactions

POSTER

Ph.D. Student: Y

Journal: JECE

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Titanium dioxide (TiO₂) photocatalysts are the most conventional due to the oxide's chemical and electronic properties, but they face limitations due to being hard to recover and their relatively large band gap energy. It's of great interest to modify these photocatalysts by spreading the nanoparticles over porous materials and adding other metal's oxides to the surface to increase the catalyst's activity and even make the reaction more selective towards certain oxygen species.

This work presents the synthesis and photocatalytic evaluation of Mn and Ti-modified SBA-15 materials. The materials were synthesized with different Mn loads and calcination heating rates. The materials were less active as the Mn load increased. After following the reaction pathways by using radical scavengers, it became apparent that this smaller activity was related to a bigger amount of superoxide radicals.

Introduction

TiO₂ is the most studied semiconductor material in photocatalysis due to its properties, but its relatively large band gap energy limits its use [1]. Moreover, its very small particles yield a relatively small surface area that gets further reduced due to their high tendency to agglomerate. The development of TiO₂-based nanocomposite materials mixed with other metallic species and dispersed over porous materials with large surface areas has been of great interest in the last years in order to overcome the limitations TiO₂ faces [1,2].

Advances in the development of manganese-based photocatalysts have occurred in the last few years. Mn is an abundant, non-toxic metal that presents itself in multiple oxidation states, yielding stable oxides with various structures and band gaps [3]. In order to increase the surface area of TiO₂-based photocatalysts, the dispersion of its particles in mesoporous silica has been reported. Some of the most popular have been SBA-15 materials due to their large surface area, moderate pore size, highly-ordered structure and high chemical stability [2].

The scope of this work is to develop and evaluate Ti and Mn-modified SBA-15 materials with different Mn loads and under different synthesis conditions. The solids were photocatalytically tested in an Acid Orange 7 (AO7, a phenolic dye commonly used as a model pollutant) aqueous suspension by exposing them under a UV/Vis light. The experiences were repeated with different radical scavengers and under N₂ insufflation to verify their activity through different reactive oxygen species (ROS). Hydroxyl radical (HO•) and superoxide anion radical (O₂•⁻) are the most common ROS [3]. O₂•⁻ is of particular interest since it acts as substrate for enzymes such as

superoxide dismutase (SOD), making way for the development of chemoenzymatic cascade systems.

Material and Methods

Metal-free SBA-15 mesoporous silica was produced by the sol-gel method as described by Zhao *et al.* [4] with tetraethylortosilicate (TEOS) as silicon source, Pluronic P123 as the structure-directing agent and HCl. The calcined SBA-15 was modified post-synthesis by the wet impregnation method, introducing 2.5, 5 and 10% wt. Mn loads via saline aqueous solutions. The resulting powders were dried and then calcined for five hours at 500 °C with two different heating rates: 4 °C and 8 °C/min. Afterwards the cycle was repeated to impregnate the materials with 20% wt. Ti by making a suspension of the previously made Mn/SBA-15 materials with an isopropanol solution of titanium n-butoxide. The resulting materials were labeled as Ti/Mn(Mn wt. load, %)/SBA-15 R(heating rate).

The degradation experiments were performed with a stirred batch photoreactor, irradiated over its top with an UV/vis LED 30 W lamp (390 nm, as shown in the Graphical Abstract). 20 mg of material were suspended in 20 mL of 20 ppm AO7 aqueous solution, first for 45 min in dark conditions to reach the adsorption/desorption equilibria and then exposed to light for 3 h. To determine the chemical path followed by each sample, the experiments were repeated with the same AO7 solutions fortified with either 8% isopropanol (HO• scavenger) or 4% chloroform (O₂•⁻ scavenger) [5]. Afterwards, the least and most active materials with chloroform as radical scavenger were tested under N₂ insufflation to further confirm the relevance of the superoxide radical pathway over the hydroxyl one in the

photocatalytic processes for those materials.

Results and Discussion

The photocatalytic evaluation of all the materials is shown in Table 1. It becomes clear that there are not any significant changes in the materials' activity as the Mn load increases when synthesizing with a heating rate of 4 °C. On the other hand, materials synthesized with an 8 °C/min heating rate yield larger activity with lesser Mn loads. Evaluation of these materials' activity with radical scavengers is then of great interest since $O_2^{\bullet-}$ is less reactive than HO^{\bullet} . As shown in Table 1, materials up to a 5% wt. Mn load show a larger reduction of activity (which becomes more largely decreased for materials synthesized with a heating rate of 8 °C/min) when adding isopropanol, thus hydroxyl-based photocatalytic pathways can be inferred for these materials. On the other hand, photocatalytic activity decreases in very similar amounts with either isopropanol or chloroform for materials with a 10% wt. Mn load, thus showing increased $O_2^{\bullet-}$ production. In order to further confirm the results from the experiments involving chloroform, the most and least active materials (Ti/Mn(2.5%)/SBA-15 R8 and Ti/Mn(10%)/SBA-15 R8, respectively) were retested insufflating N_2 in order to induce O_2 displacement. As shown in Figure 1, the activity gets remarkably reduced for Ti/Mn(10%)/SBA-15 R8 compared to

Ti/Mn(2.5%)/SBA-15 R8. Thus, the largest residual activity is that of HO^{\bullet} , yielding values very similar to those from chloroform-fortified reactions. Superoxide radical anion presence is therefore confirmed since this species is produced over reduction of molecular oxygen [6].

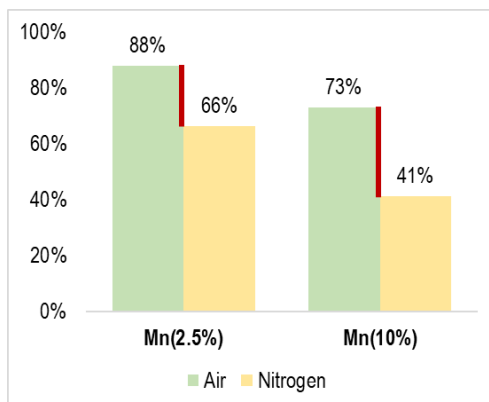


Figure 1. Reduction of activity under O_2 displacement with N_2 for Ti/Mn(2.5%)/SBA-15 R8 (left side) and Ti/Mn(10%)/SBA-15 R8 (right side). The decrease, a fraction corresponding with superoxide production, is further shown with a red line.

Table 1. AO7 (20 ppm) removal after three hours reaction under 390 nm LED lamp (%) and its relative decrease to the previous reaction after same length reaction with radical scavengers (%) for Ti(20%)/Mn/SBA-15 materials.

Heating rate	AO7 Removal			Scavenger	Removal decrease by scavenger		
	Mn(2.5%)	Mn(5%)	Mn(10%)		Mn(2.5%)	Mn(5%)	Mn(10%)
4 °C/min	79.02%	81.36%	77.30%	Isopropanol ^a	47.04%	49.60%	61.02%
				Chloroform ^b	29.32%	26.45%	57.53%
8 °C/min	88.05%	72.99%	73.15%	Isopropanol ^a	76.79%	54.33%	56.74%
				Chloroform ^b	12.22%	6.74%	56.92%

^a Hydroxyl radical scavenger.

^b Superoxide anion radical scavenger.

Conclusions

Mn and Ti-modified SBA-15 materials were synthesized with different metal loads and heating rates. As the Mn load increased, the materials became less effective when it came to AO7 removal. On the other hand, when focusing on following the reaction pathways by adding radical scavengers to the suspension, it was proven that superoxide activity increased with Mn load regardless of the heating rate. These results can lead to synthesis optimization by making the reactions more selective towards certain radicals, either for simple pollutant removal or the development of chemoenzymatic cascade systems.

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