Sodium Titanate Synthesis For The Photocatalytic Degradation of NO

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Research Article

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Abstract

The synthesis and characterization of sodium titanates (ST) and its evaluation in the photocatalytic reduction of nitric oxide (NO) is described in this contribution. The materials were synthesized by an hydrothermal route using the following parameters; 5 M NaOH concentration used as TiO_2 mineralizer agent, under 170 °C for 48 hours, and a dose of TiO_2 of 0.06 mg/mL (expressed as the mass ratio of TiO_2 /mL with respect to NaOH); resulting in tri- and hexa- ST. A nanotubular morphology was observed for the ST as proved by scanning electron microscopy (SEM) and a subsequent heat-treatment at 400 °C allowed a complete transformation of tri- to hexa- sodium titanates to modify the bandgap. The obtained ST were impregnated with Ag^+ and Zn^+ cations, respectively (ST-Ag, ST-Zn), to tune the bandgap of the materials. XPS analysis of the ST-Ag materials showed evidence of metallic Ag pointing to the formation of silver nanoparticles, whereas for ST-Zn oxide phases were mainly spotted. The materials were evaluated for the photocatalytic reduction of NO using a reactor fed with a continuous flow rate of NO, generated *in situ*, at a flow rate of 280 ml/min using nitrogen and a 253 nm wavelength UV irradiation source. The photocatalytic tests showed that pristine ST (tri and hexa-titanate) was the photocatalyst that displayed the best performance in the reduction of NO with respect to the impregnated samples (ST-Ag, ST-Zn). Maximum efficiencies of 80% degradation were reached when using 1 g of photocatalyst with a flow of 280 ml/min and a lamp of 253 nm.

Introduction

Photocatalysis is a process with important applications in environmental remediation and energy production. Nowadays, TiO_2 is the photocatalyst more applied in several process for treating wastewater, generation of hydrogen, degradation of pollutants in the atmosphere and in the generation of electricity by photoelectron-chemical conversion of solar energy (Carbajo et al., 2017; Chiarello et al., 2017; Yan et al., 2013;). However, the re-combination of (e^-h^+) pair in the surface of TiO_2 when the photocatalytic process occurs and the bang gap of 3.2 eV, limits the use of a small fraction of solar irradiation (approximately 4%) in form of UV light, this has motivated the quest of novel photocatalysts or strategies to modify TiO_2 to overcome these limitations (Carbajo et al., 2017). For instance, Fe-doped TiO_2 material has been prepared avoiding charge recombination (Wu and van de Krol, 2012). The Fe-doped TiO_2 photocatalyst was evaluated for photo-oxidation and photo-reduction of NO by the presence of Fe and oxygen vacancies that suppresses the formation of NO_2 . In the mentioned work, three issues were concluded: NO_3^- generation via photo-oxidation, suppression of NO_2 and the NO photo-reduction to obtain N_2 and O_2 . However, the poisoning of the catalysts was observed as ascribed to the formation of NO_3^- in the surface of the material blocking the oxygen vacancies. Other attempts include the use of titanium-based inorganic perovskites, such as SrTiO_3 decorated with SrCO_3 , which was tested to degrade NO by photocatalysis (Jin et al. 2018). Charge recombination was avoided in these materials by using a co-photocatalyst strategy (SrTiO_3 - SrCO_3). In the same line, Parayil et al., (2015) employed nitrogen-doped sodium titanate nanotubes (STT) in the photocatalytic conversion of CO_2 . Doped and undoped STT

prepared by hydrothermal treatment showed a promising performance to reduce CO_2 to CH_4 . ST can be modified by acid washing and thermal treatments to enhance their photocatalytic activity (Nguyen and Bai, 2015). Other modifications involve doping with noble metals to degrade organic matter (El Rouby et al., 2017). Their morphology is appropriate to increase the catalytic and photocatalytic activity due to tubular structure and surface areas $> 200 \text{ m}^2/\text{g}$ (Machorro López et al., 2021). Then, the use of ST in the degradation of NO_x is a potential option for NO_x photo-reduction with the subsequent generation of N_2 and O_2 in comparison with the photo-oxidation obtained in other studies (Nguyen and Bai, 2015). Alternative strategies have been implemented to modify the band gap and avoid the recombination of (e^- - h^+) pair. Ibukun and Jeong (2020) achieved the TiO_2 modification with silver to avoid the abovementioned issues. These authors reported that the modified TiO_2 was active in the visible region; moreover, degradation kinetic of methyl blue was increased. Turkten and Bekbolet (2020) achieved the modification of TiO_2 with ZnO to avoid the recombination of (e^- - h^+) pair and to extend the bandgap of the photocatalyst to the visible region. The material was evaluated in the degradation of humic acid demonstrating its effectivity due to the band gap modification. Nevertheless, the modification of titanium-related materials such as ST with Ag^+ and Zn^+ has been poorly investigated and tested in environmental remediation studies.

NO_x , SO_x and other pollutants have a serious role in the atmospheric process of pollution. Nitric oxide (NO) is the primary pollutant emitted with a small proportion of nitrogen dioxide (NO_2) although NO is oxidized in the atmosphere to NO_2 . NO_2 is responsible for ozone (O_3) generation. Since the 80's, the three-way catalysts are used in automobiles to mainly decrease NO_x levels in air (Koltsakis et al., 1998). However, the growth of automobiles in the worldwide has occasioned negative effects in the environment, although, in several countries electric cars and legislation already is a reality to transition of zero emissions automobiles. However, in other countries of America and Africa this transition to electric cars is seen so far. Moreover, industrial emissions are another principal source of air pollution. Then, the NO_x emission from anthropogenic and natural process is high. NO_x are pollutants with significant effect in the atmosphere and the total environment. NO , N_2O and NO_2 are the three well-known NO_x species mainly generated via anthropogenic processes. Despite the efforts implemented in the abatement of these gases, the presence of NO_x in the air is high because NO_x are principally originated from fuel combustion. In the 2020 was demonstrated an excellent way to decrease the worldwide pollution emissions: pandemic situation brought itself the solution when people stopped their mobility. For instance, in China a decreasing of NO_x emissions occurred: NO_x emissions decreased 50% in east China in the period of January 23rd to February 9th (Zhang et al., 2020). Nevertheless, economic affectations were evident and, while the economic transition to less human mobility do not apply, the abatement technologies of pollutants must be improved. Therefore, in this work the preparation of ST by hydrothermal treatment and their evaluation in the photocatalytic degradation of NO is studied. In particular, the ST were prepared with a low concentration of NaOH . Moreover, the modified ST with silver and zinc oxide were tested to demonstrate their efficiency in the photo-reduction of NO to generate N_2 and O_2 .

Materials And Methods

Synthesis of ST

ST was synthesized by a modified Kasuga procedure (Kasuga et al. 1998). Briefly, 3 g of commercial TiO_2 was placed with a NaOH solution (2.5 or 5 M) at room temperature for 24 h with continuous magnetic stirring. Furthermore, the mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 170°C for 48 h. Finally, the obtained product was recovered by filtration and washed several times with distilled water until reached a pH 7 and dried at 110°C . Additionally, a batch of dried samples was annealed at 400°C using a temperature ramp of $1^\circ\text{C}/\text{min}$ to determine its effect on the ST phases, the samples were labeled as CST, where the C stands for “calcined”.

Synthesis of modified ST

Modified ST materials were synthesized to modify the band gap and avoid the recombination of (e^-h^+) pairs to increase their photocatalytic activity (Wodka et al., 2010; Albiter et al., 2015). The preparation procedure was as follows: the appropriate amount of AgNO_3 or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ calculated for 5 % in weight, was dissolved in 1 mL of H_2O , and then 1 g of ST was added to the above solutions. All samples were dried at 100°C and calcined at 400°C for 2 hours with a temperature ramp of $10^\circ\text{C}/\text{min}$. The obtained samples were denoted as ST-Ag5 and ST-Zn5.

Characterization

The crystalline structure of the samples was analyzed by a Bruker D8 Advance X-ray Diffractometer (XRD) with a $\text{Cu-}\lambda$ radiation ($\lambda = 0.15406 \text{ \AA}$) with a Nickel filter operating at 40 kV and 40 mA. The data were collected in the 2θ range from 5° to 50° with a scan rate of 0.02° . The morphology of the samples was observed by SEM (Jeol, JSM-6510 LV), while elemental identification was carried out by energy-dispersive X-ray analysis (EDX). Transmission Electron Microscopy (Jeol, JEM-1400Plus) was also used for the morphological studies. The surface chemical bonding was analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific, K-Alpha) equipped with Al K α X-ray source at energy of 1486.6 eV measuring points of $200 \times 200 \text{ mm}$. Calibration was confirmed by adventitious carbon C1s at 285 eV. Spectrum deconvolution was carried out using a Gaussian model. The thermal stability of the samples was investigated by thermogravimetric analysis (TGA) in a Netzsch STA 449 F5 Jupiter from room temperature to 900°C . The samples were heated with $10^\circ\text{C}/\text{min}$ from room temperature to 900°C , under a nitrogen flow of 50 mL/min. The optical characterization of the samples was carried out by UV-Vis diffuse reflectance with a Shimadzu UV-2600 spectrophotometer. The diffuse reflectance spectra (DRS) were recorded in the wavelength range of from 200 to 800 nm.

Photocatalysts evaluation

NO_x generation was carried out using HNO_3 and metallic copper according to reaction 1 and 2:

The NO generation was carried in the absence of oxygen in the reaction 2. Cu and HNO₃ were mixed in a Buchner flask to generate NO. N₂ was used as carrier gas using a flow of 280 mL/min. Gaseous flow passed through a photocatalysis reactor that consists of a flask with a monochromatic pencil lamp of 253 nm, where 1000 milligrams of the photocatalysis in powder form was loaded. The photocatalytic activity of the samples was evaluated in an experimental arrangement shown in the Fig. 1, where a continuous flow of N₂ (used as carrier of *in-situ* produced NO) was fed in the photocatalytic reactor. Mixture of gases were transported to the abatement chamber passing through the surface of the photocatalyst and irradiated at 253 nm (UV) from monochromatic source inside the chamber for 10 minutes. An AMPRO analyzer measured the concentration of the gas products.

Previous to photocatalytic evaluation, a statistical analysis of variance (ANOVA) of initial NO concentration was carried out (Table 1). Twenty experiments were recorded without the use of a photocatalyst. Likewise, a t-test was performed for samples assuming equal variances. The previous analysis allowed to estimate a standard deviation (σ) = 71.67 and a mean = 641 ppm of initial concentration NO with an interval of ± 31.41 ppm. From this, the degradation was measured with respect to the obtained values.

Table 1. ANOVA for the production of NO.

Origin of the variations	Sum of squares	Degrees of freedom	Average of squares	F-value	Probability
Between group	1584.2	1	1584.2	4.4138	0.5924
Whitin-group	96016.6	18	5334.2		
Total	97600.8	19			

Results And Discussion

In Fig. 2, X- ray diffraction (XRD) XRD patterns of TiO₂, ST, CST and modified ST are displayed. Two principal crystalline planes (1 0 1) and (1 1 0) were identified corresponding to anatase and rutile in the TiO₂ sample. However, the patterns of the particles obtained after the hydrothermal treatment, pointed to the fading of the characteristic peaks of P25 powder and new peaks corresponding to ST appeared. The diffraction peaks ~ 10, 24, 28 and 48 2 θ , could be clearly identified and are in agreement with a titanate layered structure (Fig. 2(a-e)). The broad peaks at 10 and 28 2 θ correspond to interlayer spacing in layered titanates and revealing the nanotube structure (Hernández and Medina 2015; Vattikuti et al. 2018). The peaks at 24 and 48 2 θ indicate the presence of hydrogen and sodium trititanates. Considering these facts, the XRD patterns can be assigned to trititanate (H,Na)₂Ti₃O₇ with different interlayer spacing; for

example, Ti_6O_{13} , Ti_6O_{12} , and Ti_9O_{18} . Diffractogram of thermally treated ST was similar to that of non-calcined ST (Fig. 1(d)). There is a modification in the low angle, $10^\circ 2\theta$ corresponding to a partial collapse in the tubular structure from thermal treatment (Lee et al., 2007). The deterioration of the tubular structure may be attributed to the dehydration of inter-layered OH radical which led to contraction and breaking of tubes structures. During the annealing treatment, the chemical bonds such as H_2O and $-\text{OH}$ are removed from the titanate structure, driving to the change of crystalline form and, at the same time, degrading the nanotube morphology. Figures 2(a) and 2(b) present the diffractograms of the bare and catalysts loaded with Ag or Zn (ST + Zn5 and ST + Ag5), where sodium titanate was the main observed phase. Due to the low concentration of co-catalysts, there is an absence of Ag or Zn species reflections in the patterns. In the case of ST + Ag5 pattern the widening of signals at low angles occurs. However, signals associated to Ag in the diffractogram at 38° and 44° were not spotted (Barrocas et al., 2016). A change at 10° signal was observed in the ST + Zn5 diffractogram that could be attributed to incomplete transformation of structural nanotubes; though, there is an increase in 28° signal of (3 1 0) plane characteristic of Zn. At 2θ of 47° a characteristic plane (2 0 0) of anatase disappeared. Three planes (0 1 1), (3 0 1) and (2 0 1) evidence the transformation of TiO_2 to ST, respectively. Titanate specie was modified changing the NaOH concentration from 2.5 to 5 M and time of 24 to 48 hours (Fig. 1).

SEM analysis

According to Fig. 3 the morphology of ST depends on NaOH concentration and time in the hydrothermal treatment. Agglomerated particles were appreciated in the Figs. 3a and 2b corresponding to ST synthesized from 2.5 M NaOH solution and 24 hours at 170°C . In contrast, Figs. 3c and 3d show tubular particles of ST. Those samples were obtained with high NaOH concentrations during 48 hours of hydrothermal treatment. Tubular aspects are related with an inter-layer coordination of non-coordinate Ti and O atoms (Saponjic et al. 2005; Morgan et al. 2008); these micrographs exhibit formation of tubular structures. The length of the obtained ST is up to few micrometers and ~ 200 nm width. The Figs. 3e and 3f correspond to ST + Ag5 and ST + Zn5, respectively. It can be noted that in both cases, there is a loss of the tubular structure due to thermal treatment during the impregnation process.

EDX analysis is showed in the Table 2. Theoretical, $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_7\text{O}_{13}$ have a $\text{Ti}/\text{Na} = 1.5$ and 3, respectively, while the O/Ti are 2.3 and 2.16. Values of Ti/Na and O/Ti in the Thermal treatment did not display a significant effect in the composition of ST, although, phase transition to anatase and rutile has been previously reported (Nguyen and Bai, 2015), that could be related to the loss of Na atoms from the ionic substitution of Na^+ by H^+ when the washing is carried out to reach a pH of 7; although, the washing was conducted only with distilled water. When Ag is impregnated in the ST material, Ti/Na increased while O/Ti decreased pointing to an ionic exchange of Na from Ag. When ST is modified with Zn, Ti/Na increased possibly from the ionic exchange of Na by Zn; however, O/Ti kept indicates the formation of ZnO in the ST. XPS analysis was conducted to verify this hypothesis (Fig. 4).

Table 2
Elemental composition of ST synthesized determined by EDX.

Sample	Elemental composition, %					Ti/Na	O/Ti	Ti/M M = Ag, Zn
	Ti	Na	O	Ag	Zn			
TiO ₂	35.00	0	65.00	0	0	-	1.85	–
ST	45.03	8.9	46.07	0	0	5.05	1.02	–
CST	45.79	7.59	46.61	0	0	6.03	1.01	–
ST + Ag5	47.10	8.26	39.48	5.16	0	5.70	0.83	9.12
ST + Zn5	45.57	5.63	46.58	0	2.22	8.09	1.02	20.52

ST and CST XPS survey spectra are similar indicating that chemical changes do not occur from thermal treatment of ST. For ST + Ag5 and ST + Zn5 signals of Ag and Zn appeared in a significant intensity. Quantification by XPS of ST samples is displayed in Table 3.

Table 3
Elemental composition of ST determined from XPS.

Samples	Elemental composition, %					Ti/Na	O/Ti	Ti/M M = Ag, Zn
	Na	Ti	O	Ag	Zn			
ST	13.67	27.96	58.37	0	0	2.04	2.08	–
CST	13.64	28.60	57.76	0	0	2.09	2.01	–
ST + Ag5	11.82	22.36	57.70	8.10	0	1.89	2.58	2.76
ST + Zn5	15.19	26.25	50.81	0	7.75	1.72	1.93	3.40

Values of Ti/Na and O/Ti ratios in ST indicate the predominant formation of sodium trititanate being the main phase from the hydrothermal treatment applied. XPS analysis of modified ST indicates the above in Table 3: ionic exchange of Na⁺ by Ag⁺ and ZnO formation. As expected, the values of elemental composition of Table 3 are different with respect to Table 2 due to the difference in the volume of analysis in each technique. Analysis from XPS guarantees the surface inspection of the samples. Surface composition change in the calcined and modified ST was expected; however, in CST composition practically this change did not occur. In the modified ST a slight decrease in the Ti/Na ratio was observed due to migration of Na atoms from the inner part of the sample to the surface originating an increase of Na composition in the surface and a change in the surrounding chemical (Fig. 5).

Characteristic signals of Ti at 459 and 465 eV that corresponds to 2p_{3/2} and 2p_{1/2} are showed in Fig. 5. Signals area attributed to Ti⁴⁺ ions forming an octahedral structure of titanates (Kurra et al. 2019). There is a doublet signal in the Fig. 5a that correspond to Ti2p_{3/2} and Ti2p_{1/2} with binding energy at 465 eV (Ti2p_{3/2}) and 459 (Ti2p_{1/2}) (Coelho et al., 2016). Na substitution by Ag and Zn was corroborated by XPS.

In Fig. 5a the Ti signals of ST and CST appear in the same binding energy while the Ti signals in ST + Ag₅ and ST + Zn₅ are moved to lower energies indicating that the incorporation of the mentioned atoms in the ST occurred. The same behavior was observed in the case of Na spectra analysis which shows a slight shift for modified ST. At 530 eV the signal of O 1s appears in all of the ST pointing to the formation of O²⁻ oxygen-titanium bonds (Hernández-Hipólito et al. 2014). In Fig. 5a a shifting in the Ti2p band corresponding to ST + 5Ag; approximately, 0.49 eV units are moved to low energy in comparison to ST and CST. This shifting is attributed to ions substitution of Na by Ag indicating from the movement of electrons in a longer distance at Ti nucleus in the atomic expansion of Ti (Barrocas et al. 2016). In the case of ST and CST signals appear at 1072 eV indicating the presence of ions Na in the titanate (Marciniuk et al. 2014). Moreover, in the case of the Ag3d a difference of 6eV between Ag3d_{5/2} (368 eV) and Ag3d_{3/2} (374 eV) is characteristic to metallic state of Ag (Duan et al., 2017). In Fig. 5d the XPS spectra of ST + 5Zn is showed emphasizing the signals at 1021 and 1044 eV. Division of orbitals of Zn2p in the ZnO is observed (Wang et al. 2009). A shifting of 0.81 eV in the Ti2p occurs pointing to a change in the Ti environment in coordination with Zn being modified the ionic radius of Ti. In this case, the presence of octahedral and tetrahedral titanium is possible (Cho et al. 2014; Wang et al. 2009). However, the samples in this study only show the octahedral structure where the metallic atoms do not modify the principal structure of ST. XPS analysis show that ST is not affected in the elemental composition from the thermal treatment at 400°C. SEM images and the EDS analysis corroborate the above mentioned, although, the tubular structure in the ST collapses. ST + 5Ag and ST + 5Zn display a different behavior because the binding energies indicate that the ST are not forming binding to the metallic elements. Additionally, the ionic exchange of Na by Zn and Ag occurs. In TEM images are appreciated the morphology of the samples prepared herein (Fig. 6).

TEM images shows the tubular structure of ST (Fig. 5a) although this morphology collapses when is treated at 400°C (Fig. 6b). In the case of modified ST, small particles are appreciated in each case demonstrating the formation of nano particles from the ionic exchange. In order to explain the collapse of morphology thermogravimetric (TGA) analysis was employed. In Fig. 7 the TGA/DSC analysis of the samples is showed.

Thermogravimetric curves of the obtained ST materials are displayed in Fig. 7. The greater part of the weight loss occurs at lower temperatures, where the dehydration of physisorbed water takes place. The single stage weight loss of roughly 10% occurs up to 200°C. This process is reflected as an endothermic peak on a DSC curve. After this temperature the weight slowly and continuously decreases nearly up to 700°C. At $T \leq 300^\circ\text{C}$ the dehydration of interlayered OH groups could reduce the interlayer distance but does not destroy the tubular shape. When temperature $> 300^\circ\text{C}$, the dehydration of interlayered OH groups induced the change of crystalline form and, at the same time, the nanotube morphology is destroyed. A broad exothermic peak in a temperature range from 300 to 800 C on the DSC curve could indicate that the synthesized ST, loose interlayered OH groups in a broader range while interlayered OH groups remain in the structure up to 600°C or the cleavage of both type of OH groups occurs simultaneously. Between 200–300°C an exothermic reaction occurs attributing this process to hexa-tri-titanate transformation (Lee

et al. 2007). At 400–600°C an endothermic process is observed that means the collapse of tubular structure forming spherical particles.

A comparison of prepared ST using UV-vis spectroscopy demonstrates the absorbance of ST with and without modifications in a range of 600 – 200 nm (Figure not showed). Figure 8 shows the UV-vis spectroscopy modified with the Kubelka-Munk function showing a high absorption between 325–340 nm to ST and CST while for ST + Ag5 and ST + Zn5 the absorption is observed at 355 nm. TiO₂ spectra shows the absorption at 350 nm indicating a shifting of bands for the prepared ST from the dispersion of photons by defects in the crystals of ST (Benzarouk et al. 2012). Eg-values are observed in the Table 3.

Table 3
Optical Eg obtained from the Kubelka-Munk function applied to DRS spectroscopy of prepared ST.

Sample	Eg (eV)
TiO ₂	3.5
ST	3.8
CST	3.6
ST + Ag5	3.4–3.5
ST + Zn5	3.4–3.5

Eg-TiO₂ values resulted modified when it was transformed to sodium titanate from 3.5 to 3.8 eV. Moreover, Eg-CST value decreased at 3.6 due to recrystallization and morphology change from the thermal treatment. Impregnation of ST with Ag and Zn promoted a slight change of Eg due to the Burstein-Moss effect. The change in the absorption bands was caused by increasing of carrier charges and the blocking of low energy transitions from the doped and calcined treatment of ST. This promoted an increasing of Fermi level modified the Eg (Achour et al. 2007). It is preferable that the energetic levels decreasing to active the photocatalyst making more large the interval of light that can be useful, UV and visible.

NO abatement

According to reactions 1 and 2, NO was produced by mixing certain amounts of Cu and HNO₃ obtaining a maximum concentration of 641 ppm in average. NO photo-degradation using ST are showed in the Fig. 9 and compared with the use of TiO₂.

Figure 9a shows the NO concentration in function of amount of copper in the reaction 2. Practically, there is not degradation of NO (conversion to NO₂) for the exposition under UV light (253 nm). It is important to note that the NO concentration proved in the present work were higher than those reported in previous

reports, for instance, Ma et al., (2015) achieved the photocatalysis process with 400 ppb of NO; Duan et al., (2017) used 450 ppb of NO. Concentration tested herein was selected considering the maximal concentration of NO emission in a car with an air:fuel ratio 14.64:1 (by mass) that is less than the stoichiometric level (Dey and Mehta, 2020). TiO_2 exhibited a degradation percentage of around 50% with an initial charge of 0.2 and 0.4 g, although, when the amount of photocatalyst increased, the NO degradation remains unchanged. This means that TiO_2 showed a capacity to decrease the NO concentration until 320 ppm being significance in the total emissions in a car with the above characteristic of air:fuel ratio. Moreover, higher charges of TiO_2 are not favorable for the photo-reduction of NO: with 0.6, 0.8 and 1 g of TiO_2 an increase of C/Co occurred possibly by phenomenon of adsorption. Namely, when NO is on the photoreactor TiO_2 adsorb it blocking sites for the photocatalysis process. Carrera et al., (2007) reported a similar behavior: when the time of exposition passed the NO concentration increased possibly also by the blocking of photocatalytic sites in the TiO_2 surface when a low NO concentration (50 ppm) was tested. Other possible reason is the non-homogeneous distribution of the sample in the photo reactor that prevented the usage of total of the area of the TiO_2 . However, this explanation is opposite with the other photocatalyst materials because ST, with and without modification, showed higher performance increasing the NO photo-degradation with higher charges of photocatalyst. The most efficient synthesized photocatalyst was ST using 1.0 g in the experiments. NO degradation occurred in stages and is relatively similar to other photocatalyst used (65% percentage of degradation). Compared with the same material load, CST degraded 62% of NO, while TS + Ag5 and TS + Zn5 showed a degradation percentage of 45% and 40%, respectively. Major percentage of NO degradation is attributable at higher surface area in ST than other photocatalysts. Possibly, the thermal treatment in the modified ST affected the performance reducing the surface area and the active sites to achieve the photocatalytic process. This is better related to the band gap of the ST; it is consistent to say that the band gap, together with the surface area of the sample, have a greater influence on the photocatalytic effect of the synthesized materials. Then, the thermal treatment in the ST was not suitable to degrade NO.

One of the possible routes for NO photoreduction is described as catalytic sites which tetrahedrally coordinated Ti is found on the surface. This species has been reported by Anpo et al. (1997) as a catalytic site that favors the decomposition of NO to N_2 and O_2 using Ti-modified zeolites. Since most of the Ti ions on the surface of the photocatalyst have a 5 coordination, a single oxygen vacancy could lead to the formation of a reducing site. Wu and van de Krol (2012) described NO reduction mechanism where NO molecules are captured in sites where oxygen vacancies working as photo-catalytic sites. In the work of Nguyen and Bai (2015) photo degradation of NO_x was pointed out oxidant the NO and NO_2 using ST treated with acid while in the present work the photo reduction of NO was demonstrated. Moreover, the adsorption of NO did not occur in the conditions herein. Experimental data shows the highest degradation percentages for synthesized photocatalysts.

Conclusions

This work demonstrated the preparation of sodium titanate from hydrothermal treatment as well as the modification of this photocatalysts by thermal treatment and impregnation of zinc and silver to modify their photocatalytic properties. Mixture of tri and hexa titanates were obtained with low concentration of alkali being important to generate an environmental friendly process. Moreover, photocatalytic activity of sodium titanates synthesized from hydrothermal treatment was tested to degrade NO by reduction. Sodium titanate was modified with Ag and Zn to increase the photocatalytic activity; however, the major activity to degrade NO was reported with the sodium titanate without modification. Likely, this high activity to degrade NO occurred from the number of active sites in the photocatalyst in comparison with the modified sodium titanates. Photo reduction of NO_x occurred in comparison with other works to degrade this pollutant. This means a advantage due to not-generation of subproducts in the reaction being the nitrogen and oxygen only generated.

Declarations

Ethic approval and consenting to participate: not applicable.

Consent to publication: not applicable.

Availability of data and materials: no applicable.

Competing interest: there are not competing interests.

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Author's contribution: M. Cueto Bastida achieved the experimental work in his master thesis; Y. Maldonado characterized and interpreted the results from XRD technique; Y. Reyes Vidal suggested several issues in the work; M. Solis and E Coutino achieved a deep discussion of results; F. Espejel Ayala proposed the idea and obtained the funding to developed the project and prepared the manuscript.

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Figures

Figure 1

Schematic representation of the experimental arrangement of the continuous flow system for photocatalytic degradation of NO.

Figure 2

XRD patterns of (a) = ST+Zn5, (b) = ST+Ag5, (c) = CST, (d) =ST, (e) = TiO2, (Anatase= *, Rutile= $\square$, Titanate= $\diamond$).

Figure 3

SEM images of materials prepared in this work. a) and b) ST synthesized from 2.5 M NaOH solution and 24 hours at 170 °C; c) and d) ST obtained from 5 M NaOH solution during 48 at 170 °C; e) ST+Zn5; f) ST+Zn5.

Figure 4

Survey spectra of ST prepared. a) ST synthesized from 2.5 M NaOH solution and 24 hours at 170 °C; b) sodium titanate calcined at 400 °C c) ST+Zn5, sodium titanate impregnated zinc oxide d) ST+Ag5, sodium titanate impregnated silver.

Figure 5

High resolution XPS spectra for a) Ti, b) Ag, c) Na and d) Zn in ST samples.

Figure 6

TEM images of a) ST, b) CST, c) ST+5Ag and d) ST+5Zn.

Figure 7

TGA/DSC of ST prepared with 2.4 M NaOH concentration, 24 h and 170 °C.

Figure 8

Normalized UV-vis reflectance diffuse spectra (DRS) of ST prepared and TiO₂.

Figure 9

a) NO concentration in function of amount of Cu with and without UV light. a) photocatalytic degradation of NO from 0.2 g to 1.0 g with 0.2 g increase on average using different photocatalysts prepared herein.