Synthesis of Sodium Titanates and Their Use in 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 their evaluation in the photocatalytic reduction of nitric oxide (NO) are described herein. The materials were synthesized by a hydrothermal route using 5 M NaOH as the mineralizer agent and a TiO$_2$ content of 0.06 mg/mL (expressed as the mass ratio of TiO$_2$/mL of NaOH), at 170 °C for 48 hours, resulting in sodium tri- and hexa-titanates. A nanotubular morphology was observed for the ST, as proved by scanning electron microscopy (SEM); a subsequent heat-treatment at 400 °C allowed a complete transformation of sodium tri- to hexa-titanates and an increase in bandgap. The obtained ST were impregnated with Ag$^+$ and Zn$^+$ cations, ST-Ag and ST-Zn, respectively, to tune the materials’ bandgap. 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 of 280 mL/min using nitrogen and a 253 nm UV irradiation source. The photocatalytic tests showed that pristine ST (tri- and hexa-titanates) displayed better performance in the reduction of NO with respect to the impregnated samples (ST-Ag, ST-Zn). Maximum degradation efficiencies of 80% were achieved when 1 g of photocatalyst was used with a flow of 280 mL/min and a 253 nm UV lamp.

Introduction

Photocatalysis is a process with important applications in environmental remediation and energy production. Nowadays, TiO$_2$ is the more used photocatalyst in several processes, such as wastewater treatment, generation of hydrogen, degradation of pollutants in the atmosphere, and generation of electricity by photoelectron-chemical conversion of solar energy (Carbajo et al., 2017; Chiarello et al., 2017; Yan et al., 2013). However, the recombination of (e$^-$-h$^+$) pair in the surface of TiO$_2$ when the photocatalytic process occurs and the band 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 photooxidation and photoreduction 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 photooxidation, suppression of NO$_2$ and the NO photoreduction 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 cophotocatalyst 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 m²/g (Machorro López et al., 2021). Hence, the use of ST in the degradation of NOx is a potential option for NOx photoreduction with the subsequent generation of N₂ and O₂ in comparison with the photooxidation obtained in other studies (Nguyen and Bai, 2015).

Alternative strategies have been implemented to modify the bandgap and avoid the recombination of (e⁻h⁺) pair. Ibukun and Jeong (2020) achieved the TiO₂ modification with silver to avoid the abovementioned issues. These authors reported that the modified TiO₂ was active in the visible region; moreover, degradation kinetic of methyl blue was increased. Turkten and Bekbolet (2020) achieved the modification of TiO₂ with ZnO to avoid the recombination of (e⁻-h⁺) pair and to shift the bandgap of the photocatalyst to the visible region. The material was evaluated in the degradation of humic acid demonstrating its effectiveness due to the bandgap modification. Modification of titanium-related materials such as ST with Ag⁺ and Zn⁺ has been investigated and tested in environmental remediation studies; nevertheless, their use in as photocatalyst to degrade NOx has not been implemented.

NOx, SOx and other pollutants have a serious role in the atmospheric process of pollution. Nitric oxide (NO) is the primary pollutant emitted from combustion sources, together with a small proportion of nitrogen dioxide (NO₂), although NO is oxidized in the atmosphere to NO₂. NO₂ is responsible for ozone (O₃) generation. Since the 80s, three-way catalysts are used in automobiles to mainly decrease NOx levels in air (Koltsakis et al., 1998). However, the growth of automotive industry worldwide has caused negative effects in the environment, although in several countries electric cars and legislation are already a reality for the transition to zero-emission cars. However, in other countries in the Americas and Africa this transition seems still far away. Furthermore, industrial emissions are another principal source of air pollution. Hence, the NOx emission from anthropogenic and natural process is high. NOx are pollutants with significant effect in the atmosphere and the global environment. NO, N₂O and NO₂ are the three well-known NOx species mainly generated via anthropogenic processes. Despite the efforts made to reduce these gases, the presence of NOx in the air remains high because NOx are mainly produced by the combustion of fuels. In 2020, an excellent way to decrease pollutant emissions worldwide was demonstrated: the pandemic situation itself brought the solution when people stopped their mobility. For instance, in China, a decrease in NOx emissions was observed: NOx emissions decreased by 50% in East China in the period from January 23 to February 9 (Zhang et al., 2020). Economic impacts were evident; nevertheless, as long as the economic transition to less human mobility is not implemented, pollution reduction technologies must be improved. Therefore, this work studied the preparation of ST by hydrothermal treatment and their evaluation in the photocatalytic degradation of NO. In particular, ST were prepared with a low concentration of NaOH. In addition, silver and zinc oxide modified ST were tested to demonstrate their efficiency in the photoreduction of NO to generate N₂ and O₂.

Materials And Methods
Synthesis of ST

ST were 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, 500 mL) at room temperature for 24 h with continuous magnetic stirring. Then, the mixture was transferred to a 1L 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 pH 7 was reached, then it was dried at 110°C. Additionally, a batch of dried samples was annealed at 400°C in air using a temperature ramp of 10°C/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 bandgap 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 Zn(NO$_3$)$_2$-6H$_2$O, calculated for 5 % in weight, was dissolved in 1 mL of H$_2$O, 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°C/min. The obtained samples were denoted as ST-Ag5 and ST-Zn5.

Characterization

The crystalline structure of the samples was analyzed by X-ray diffraction using a Bruker D8 Advance X-ray Diffractometer (XRD) with a Cu-λ radiation (λ = 0.15406 Å) 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 using a JSM-6510 LV SEM (JEOL). The elemental analysis 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), using a Thermo Scientific K-Alpha instrument equipped with Al Kα X-ray source at energy of 1486.6 eV, measuring points of 200 x 200 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°C/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 range of 200 to 800 nm.

Photocatalysts evaluation

NOx generation was carried out using HNO$_3$ and metallic copper according to reaction 1 and 2:

Cu(s) + 4HNO$_3$(aq) → Cu(NO$_3$)$_2$(aq) + 2NO$_2$(g) + 2H$_2$O(l) ..............................reaction 1
3Cu(s) + 8HNO₃(aq) → 3Cu(NO₃)₂(aq) + 2NO(g) + 4H₂O(l) ........................reaction 2

In reaction 2, the NO generation was carried out in the absence of oxygen. 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 consisting of a flask with a pencil-type lamp as a source of monochromatic radiation at 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 as shown in Figure 1, where a continuous flow of N₂ (used as carrier of in-situ produced NO) was fed in the photocatalytic reactor. The mixture of gases were transported to the abatement chamber passing through the surface of the photocatalyst and irradiated at 253 nm (UV) with the monochromatic source inside the chamber for 10 minutes. An AMPRO analyzer was used to measure the concentration of the gas products.

Prior 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.

| 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                 |                    |         |             |

Table 1
ANOVA for the production of NO.

Results And Discussion

In Figure 2, X-ray diffraction (XRD) patterns of TiO₂, ST, CST and modified ST are displayed. Two main crystalline planes (1 0 1) and (1 1 0), 25.3 and 27.4 2θ respectively, were identified corresponding to anatase and rutile only 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 at ~10, 24, 28 and 48 2θ, could be clearly identified and are in agreement with a titanate layered structure, Figure 2(a-e). The broad peaks at 10 and 28 2θ correspond to interlayer spacing in layered titanates and reveal the nanotube structure (Hernández and Medina 2015; Vattikuti et al. 2018). The peaks at 24 and 48 2θ 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, Ti₆O₁₃, Ti₆O₁₂, and Ti₉O₁₈. Diffractogram of thermally treated ST was similar to that of non-calcined ST, Figure 1(d). There is a modification in the low angle 10
2θ, 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 anion which led to the contraction and breaking of tube structures. During the annealing treatment, the chemical bonds such as H₂O and −OH are removed from the titanate structure, driving to the change of crystalline form and, at the same time, degrading the nanotube morphology. Figures 1(a) and 1(b) show the diffractograms of the bare and Ag or Zn-loaded catalysts (ST+Zn5 and ST+Ag5), where sodium titanate was the main phase observed. Due to the low concentration of co-catalysts, there is an absence of reflections of Ag or Zn species in the patterns. In the case of ST+Ag5 pattern, signal broadening occurs at low angles. 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, this could be attributed to the incomplete transformation of structural nanotubes (Li et al., 2012); yet, there is an increase at 28° characteristic of (3 1 0) plane of Zn. At 2θ of 47° a characteristic peak corresponding to plane (2 0 0) of anatase disappeared. Three planes (0 1 1), (3 0 1) and (0 2 1) at 9.4, 27.5 and 48.3 2θ, respectively, evidence the transformation of TiO₂ to ST. Titanate species were modified by changing the NaOH concentration, from 2.5 to 5 M, and time was varied from 24 to 48 hours (Figure 2).

SEM analysis

According to Figure 3, the morphology of ST depends on NaOH concentration and time in the hydrothermal treatment. Agglomerated particles were observed, Figures 3a and 2b correspond to ST synthesized from 2.5 M NaOH solution and 24 hours at 170°C. In contrast, Figures 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 to an interlayer coordination of non-coordinate Ti and O atoms (Saponjic et al. 2005; Morgan et al. 2008); these micrographs exhibit the formation of tubular structures. The length of the obtained ST is up to few micrometers and ~200 nm width. Figures 3e and 3f correspond to ST+Ag5 and ST+Zn5, respectively. It can be observed that in both cases there is a loss of the tubular structure due to the thermal treatment during the impregnation process.

EDX analysis is shown in Table 3. Na₂Ti₃O₇ and Na₂Ti₇O₁₃ have theoretical values of Ti/Na= 1.5 and 3, respectively, while O/Ti values are 2.3 and 2.16. Values of Ti/Na and O/Ti in Table 2 indicate the presence of residual TiO₂, according to quantification by Rietveld analysis (results not shown). Thermal treatment did not display a significant effect in the composition of ST, although the anatase to rutile phase transition has been previously reported (Nguyen and Bai, 2015), owing 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. When Ag is impregnated in the ST material, Ti/Na increased while O/Ti decreased, pointing to a Na⁺/Ag⁺ ion exchange. When ST is modified with Zn, Ti/Na increased possibly from the ion exchange of Na with Zn; however, O/Ti indicates the formation of ZnO in the ST. XPS analysis was conducted to verify this hypothesis (Figure 4).
Table 2
Elemental composition of the synthesized ST determined by EDS.

| Sample     | Elemental composition, atomic % | Ti/Na | O/Ti | Ti/M  |
|------------|---------------------------------|-------|------|-------|
|            | Ti     | Na  | O    | Ag   | Zn   | M=Ag, Zn |
| TiO₂       | 35.00  | 0   | 65.00| 0    | 0    | -         |
| ST         | 45.03  | 8.9 | 46.07| 0    | 0    | 5.05      |
| ST+Ag5     | 47.10  | 8.26| 39.48| 5.16 | 0    | 5.70      |
| ST+Zn5     | 45.57  | 5.63| 46.58| 2.22 | 0    | 8.09      |

ST and CST XPS survey spectra are similar, indicating that chemical changes are not caused by the thermal treatment of ST. For ST+Ag5 and ST+Zn5, signals of Ag and Zn appeared with 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  |
|---------|--------------------------|-------|------|-------|
|         | Na  | Ti       | O      | Ag   | Zn   | M=Ag, Zn |
| ST      | 13.67 | 27.96  | 58.37  | 0    | 0    | 2.04      |
| CST     | 13.64  | 28.60  | 57.76  | 0    | 0    | 2.09      |
| ST+Ag5  | 11.82 | 22.36  | 57.70  | 8.10 | 0    | 1.89      |
| ST+Zn5  | 15.19 | 26.25  | 50.81  | 0    | 7.75 | 1.72      |

Values of Ti/Na and O/Ti ratios in ST indicate the predominant formation of sodium trititanate, this 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 shown in Table 4 are different with respect to Table 3, due to the difference in the volume of the analyzed sample 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, for the CST composition this change did not occur. In the modified ST a slight decrease in the Ti/Na ratio was observed, due to the migration of Na atoms from the inner part of the sample to the surface, causing an increase of Na in the surface and a change in the surrounding chemical composition (Figure 4).

Characteristic signals of Ti at 459 and 465 eV which correspond to 2p₃/₂ and 2p₁/₂ are shown in Figure 5. Signals are attributed to Ti⁴⁺ ions forming an octahedral structure of titanates (Kurra et al. 2019). Figure 5a shows a doublet signal, corresponding to Ti₂p₃/₂ and Ti₂p₁/₂ with binding energy at 465 eV (Ti₂p₃/₂).
and 459 (Ti2p\textsubscript{1}/2) (Coelho et al., 2016). Na substitution by Ag and Zn was corroborated by XPS. In Figure 5a, the Ti signals for ST and CST appear in the same binding energy, while the Ti signals for ST+Ag5 and ST+Zn5 are shifted to lower energies, indicating that the aforementioned atoms were incorporated into the ST. This same behavior was observed in the case of Na spectra analysis, showing a slight shift for the modified ST. The O 1s signal appears at 530 eV in all of the ST, indicating the formation of O\textsuperscript{2−} oxygen-titanium bonds (Hernández-Hipólito et al. 2014). Figure 5a shows a shift in the Ti2p band, corresponding to ST+5Ag, it is shifted to lower energy by approximately 0.49 eV units compared to ST and CST. This shifting is attributed to the substitution of Na with Ag ions, which indicates the movement of electrons over a longer distance in the Ti nucleus in the atomic expansion of Ti (Barrocas et al. 2016). In the case of ST and CST, signals appear at 1072 eV revealing the presence of Na ions in the titanate (Marciniuk et al. 2014). Moreover, in the case of the Ag3d a difference of 6eV between Ag3d\textsubscript{5/2} (368 eV) and Ag3d\textsubscript{3/2} (374 eV) is characteristic of the metallic state of Ag (Duan et al., 2017). Figure 5d shows the XPS spectra of ST+5Zn emphasizing the signals at 1021 and 1044 eV. The splitting of Zn2p orbitals in ZnO is observed (Wang et al. 2009). A shift of 0.81 eV in the Ti2p is observed, suggesting a change in the Ti environment in coordination with Zn, modifying 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 showed the octahedral structure where the metallic atoms do not modify the main structure of the ST. XPS analysis showed that the ST is not affected in its elemental composition with the thermal treatment at 400°C. SEM images and EDS analysis corroborate the above mentioned, although the tubular structure in the ST collapsed. ST+5Ag and ST+5Zn show a different behavior because the binding energies indicate that the ST are not forming bonds with the metallic elements. Additionally, Na ions are exchanged for Zn and Ag. TEM images show the morphology of the samples prepared herein (Figure 6).

TEM images show the tubular structure of ST, Figure 5a, although this morphology collapsed when treated at 400°C, Figure 5b. For the modified ST, small particles are observed in each case, demonstrating the formation of nanoparticles through ion exchange. Thermogravimetric (TGA) analysis was used to explain the morphology collapse. Figure 7 shows the TGA/DSC analysis of the samples.

Figure 7 shows the thermogravimetric curves of the ST materials obtained. The maximum 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. From this temperature the weight decreases slowly and continuously up to nearly 700°C. At T ≤ 300°C the dehydration of interlayered OH groups could reduce the interlayer distance, but does not destroy the tubular shape. When the temperature is >300°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 in the DSC curve could indicate that the synthesized ST lose the interlayered OH groups in a broader range, while the 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, this process is attributed to the hexa- to tri-titanate
transformation (Lee et al. 2007). At 400-600°C an endothermic process is observed, indicating the collapse of the tubular structure, forming spherical particles.

A comparison of the UV-vis spectra of the prepared ST showed the absorbance of ST with and without modifications in a range of 600-200 nm (Figure not shown). Figure 8 shows the UV-vis spectra modified with the Kubelka-Munk function, showing a high absorption between 325-340 nm for ST and CST, while for ST+Ag5 and ST+Zn5 the absorption is observed at 355 nm. TiO₂ spectrum shows an absorption at 350 nm, indicating a band shift for the prepared ST due to photon scattering caused by defects in the ST crystals (Benzarouk et al. 2012). Eg-values are shown in the Table 4.

| Sample     | Eg (eV) |
|------------|---------|
| TiO₂       | 3.5     |
| ST         | 3.8     |
| CST        | 3.6     |
| ST+Ag5     | 3.4-3.5 |
| ST+Zn5     | 3.4-3.5 |

Eg-TiO₂ value changed from 3.5 to 3.8 eV upon transformation to sodium titanate. Besides, the Eg-CST value decreased to 3.6 eV due to recrystallization and morphology change caused by the thermal treatment. Impregnation of ST with Ag and Zn promoted a slight change of Eg due to the Burstein-Moss effect (Jayaraj et al., 2002). The change in the absorption bands is a consequence of the increase of carrier charges and the blocking of low energy transitions due to the doping and calcination treatment of the ST. This promoted an increase in the Fermi level, leading to the modification of Eg (Achour et al. 2007). It is preferable that the energy levels decrease to active the photocatalyst by broadening the range 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 on average. Figure 9 shows the comparison in NO photodegradation when using ST and TiO₂.

Figure 9a shows the NO concentration as a function of the amount of copper in reaction 2. There is practically no degradation of NO (conversion to NO₂) by the exposure under UV light (253 nm). It is
important to note that the NO concentration found in the present work were higher than those reported in previous studies, for instance, Ma et al., (2015) achieved the photocatalysis process with 400 ppb of NO; Duan et al., (2017) used 450 ppb of NO. The concentration tested herein was selected considering the maximum NO emission concentration in a car with an air:fuel ratio of 14.64:1 (by mass) which is lower than the stoichiometric level (Dey and Mehta, 2020). TiO$_2$ exhibited a degradation percentage of about 50% with an initial load of 0.2 and 0.4 g; although, as the amount of photocatalyst increased, the NO degradation remained unchanged. This means that TiO$_2$ decreased the NO concentration up to 320 ppm being significant in the total emissions in a car with the above air:fuel ratio. Moreover, higher loadings of TiO$_2$ are not favorable for the photoreduction of NO: with 0.6, 0.8 and 1 g of TiO$_2$ there was an increase in C/Co possibly due to adsorption phenomena. Namely, when NO is on the photoreactor TiO$_2$ adsorbs it by blocking sites for the photocatalysis process. Carrera et al., (2007) reported a similar behavior: after exposure time, the NO concentration increased, possibly also due to the blocking of the photocatalytic sites on the TiO$_2$ surface when a low NO concentration (50 ppm) was tested. Another possible reason for this behavior is the non-homogeneous distribution of the sample in the photoreactor, which prevented the use of the total TiO$_2$ area. However, this explanation is opposite to that of the other photocatalyst materials, since ST, with and without modification, showed higher performance increasing NO photodegradation with higher loadings of the photocatalyst.

The most efficient synthesized photocatalyst was ST using 1.0 g in the experiments. The NO degradation occurred in stages and is relatively similar to that obtained when using other photocatalyst (65% of degradation). Compared to the same material loading, CST degraded 62% of NO, while TS+Ag5 and TS+Zn5 showed a degradation percentage of 45% and 40%, respectively. The higher percentage of NO degradation is attributable to a higher surface area in ST, >210 m$^2$/g (reported for Machorro López et al., 2021), than in other photocatalysts. Possibly, the thermal treatment on the modified ST affected the performance by reducing the surface area and active sites to achieve the photocatalytic process. This is best related to the bandgap of the ST; it is consistent to say that the bandgap, together with the surface area of the sample, have a greater influence on the photocatalytic effect of the synthesized materials. Therefore, the thermal treatment in the ST was not suitable for degrading NO.

One of the possible routes for NO photoreduction has been described in terms of the catalytic sites on the surface, which contains tetrahedrally coordinated Ti. 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 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 the mechanism of NO reduction where NO molecules are captured at sites where oxygen vacancies act as photocatalytic sites. In the work of Nguyen and Bai (2015), photodegradation of NOx was reported through the oxidation of NO and NO$_2$ using ST treated with acid, while in the present work the photoreduction of NO was demonstrated. Furthermore, the adsorption of NO did not occur under the conditions described herein.

**Conclusions**
This work demonstrated the not-extreme hydrothermal conditions to synthesize sodium titanates; specifically, high concentration of NaOH was avoided to generate an environmentally friendly process with low consumption of water and other reactants. Furthermore, the photocatalytic activity of sodium titanates, synthesized from hydrothermal treatment, was confirmed to degrade NO by reduction. Sodium titanate was modified with Ag and Zn to increase the photocatalytic activity; however, the highest activity to degrade NO was reported with sodium titanate without modification. This was achieved due to the different morphology of sodium titanate, nanotubular versus non-nanotubular forms of modified sodium titanate. Photo reduction of NOx was carried out and compared with other works to degrade this pollutant. The advantage over these is that no byproducts are generated in the reaction, being nitrogen and oxygen the only byproducts generated.

Declarations

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Figure 1

Schematic representation of the experimental arrangement of the continuous flow system for the photocatalytic degradation of NO.
Figure 2

XRD patterns of (a) = ST+Zn5, (b) = ST+Ag5, (c) = CST, (d) =ST, (e) = TiO2, (Anatase= *, Rutile= ☐, Titanate= ♦).
Figure 3

SEM images for the 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 hours at 170 °C; e) ST+Zn5 synthesized from 2.5 M NaOH solution and 24 hours at 170 °C; f) ST+Zn5 synthesized from 2.5 M NaOH solution and 24 hours at 170 °C.
Figure 4

Survey spectra of the prepared ST. 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 hours at 170 °C; e) ST+Zn5; f) ST+Zn5.
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, d) ST+5Ag, and d) ST+5Zn.
Figure 7

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

Figure 8

Normalized UV-vis reflectance diffuse spectra (DRS) of ST prepared and TiO2.
Figure 9

a) NO concentration as a function of the 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 the different photocatalysts prepared herein.