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Catalytic potential of titanium oxide and gold dopped titanium oxide nanoparticles in the selectivity benzyl alcohol oxidation

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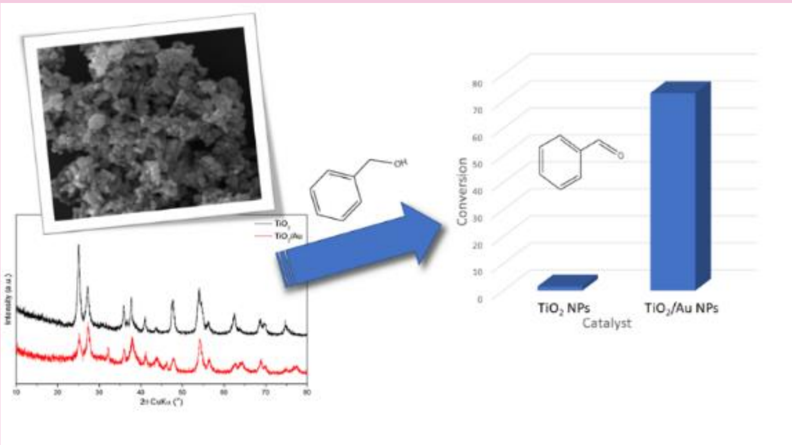
ABSTRACT: Titanium oxide (TiO_2) nanoparticles have been widely used and researched in recent years due to their wide application in several areas such as solar cells, catalysis and their chemical, non-toxic and electrical properties. Thus, this work aimed to study the catalytic potential of these nanomaterials through the oxidation of benzyl alcohol, for which TiO_2 nanoparticles synthesized by the hydrothermal method and decorated with gold nanoparticles obtained by the Turkevich method (TiO_2/Au) were used. The catalyst proved to be active for the catalysis of benzyl alcohol oxidation, with a yield of about 73% for the TiO_2/Au catalyst and 1.4% for the TiO_2 catalyst. Additionally, it was observed that the catalyst was selective, since the GC-MS and FTIR spectra showed only benzaldehyde as the final reaction product. The selective oxidation of alcohols is one of the most significant transformations in organic chemistry, as it is essential for the production of industrial intermediates.



1. Introduction

Nanotechnology field has found great application in many areas, including medicine, pharmacology and industry, and is considered to be one of the most active areas in modern material research (Chen and Mao, 2007). The increase in surface area, changes in the size and morphology of nanoparticles give them different properties, which are considered improvements when compared to the raw material. New properties, increased reactivity and potential applications in many areas of research such as antibacterial, antiviral, diagnostics, anticancer and directed to the controlled release of drugs, have led to a wide exploration of metallic nanoparticles (Bavanilatha *et al.*, 2019).

An important point regarding the synthesis of these nanostructures is the precise control of size and shape, since some properties are specifically linked to these structural characteristics (Li *et al.*, 2021). The control of these characteristics, in a hydrothermal processing, can be obtained in the nucleation and growth processes. Controlling synthesis variables, such as temperature, concentration and time, ensures greater control over the characteristics of the product to be synthesized (Arantes, 2009).

Titanium oxide is a white solid inorganic substance (Abisharani *et al.*, 2019). This semiconductor ceramic material has three main crystallographic structures: anatase, rutile and brookite, where the first two being most used because they are more thermodynamically stable (Montalvo-Quiros and Luque-Garcia, 2019). Furthermore, TiO_2 has been applied in supercapacitors, replacing ruthenium oxide due to its thermal stability, potential oxidation strength and chemical stability. This material becomes even more attractive due to its high relative abundance, low cost and safety of use (Ali *et al.*, 2020; Haider *et al.*, 2017; Kaneta *et al.*, 2019; Reddy *et al.*, 2019; Tayel *et al.*, 2018).

TiO_2 nanoparticles maintain the macroscopic material characteristics such as low cost, nontoxicity and resistance to chemical erosion, in addition to presenting catalytic and photocatalytic properties that do not exist in the macroscopic material (Cao *et al.*, 2015; S. Gupta and Tripathi, 2011; Radetić, 2013; W. Zhao *et al.*, 2021). Additionally, when associated with noble metals such as Au, Ag and Pt, it is possible to obtain excellent magnetic, optical and electrical properties (Li *et al.*, 2021; Srinivasan *et al.*, 2019; Sun *et al.*, 2017; Wang *et al.*, 2021). TiO_2 nanoparticles have wide applications in cosmetics, pharmaceuticals, skin care products, toothpastes, primarily to protect the skin from UV rays, and as a food coloring and inks (Abisharani *et al.*, 2019; Ali *et al.*, 2020; Bavanilatha *et al.*, 2019; Messaddeq *et al.*, 2019).

Surface modification is used to provide a wide range of functionality to nanoparticles, in addition to improving their specific properties (Ozdal *et al.*, 2019; Tomovska *et al.*, 2011). Thus, the photocatalytic and biological properties can be improved. One of the methodologies for functionalization of TiO_2 nanoparticles is the use of silane coupling agents. Methoxy and ethoxysilanes are the most widely used because they are easy to handle and the by-products are alcohols are noncorrosive and volatile (Dalod *et al.*, 2017; Tomovska *et al.*, 2011).

In addition, another technique that allows the modification of the properties of a nanomaterial is the synthesis of other metallic nanoparticles on top of other nanoparticles, such as the Turkevich method, a technique used to produce spherical silver nanoparticles (Gorup *et al.*, 2011).

The functionalization of nanoparticles allows the creation of hybrid nanostructures, which offer distinct advantages compared to the individual components and can also display new properties and functions for practical applications. These enhanced properties arise from the synergy between the different components due to increased interactions between them. The components of a hybrid nanostructure may be selected from a wide range of materials such as fibers, enzymes, quantum dots, conductive polymers, organometallic structures, magnetic nanomaterials. These hybrid nanostructures have enhanced active surface area, excellent adsorption capacity, easy biomolecular conjugation, improved conductivity and electrocatalytic activity. Hybrid nanostructures have been used as nanocarriers, immunological probes for the detection of biomarkers, bioanalysis, catalytical, tissue growth and healing and energy management (Borah *et al.*, 2021; Choi *et al.*, 2021; Diez-Castellnou *et al.*, 2021; Y. Gupta and Ghrera, 2021; Mitra *et al.*, 2021; Mourdikoudis *et al.*, 2021; Yang *et al.*, 2021; Zare and Sarkati, 2021; Zheng *et al.*, 2021).

The TiO_2 nanoparticles use of TiO_2 nanoparticles in several areas of science has grown a lot in recent years. It is noteworthy their use in the medical area solar cells and photocatalysis (Ananthakumar *et al.*, 2016; Kafshgari and Goldman, 2020; McNamara and Tofail, 2017; Wu *et al.*, 2020). In recent studies, X.-F. Zhang *et al.* (2019) concluded that TiO_2 nanoparticles have their photocatalytic activity improved by modifying nano-TiO_2 with noble metals, obtaining conversion rates higher than 60% in the conversion of benzyl alcohol into benzaldehyde. Lin *et al.* (2018) also observed a high photocatalytic activity in lanthanide-doped TiO_2

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nanoparticles in dye degradation. Although TiO_2 nanoparticles and composite nanomaterials present high photocatalytic activity as explained, there is still a challenge regarding the use of TiO_2 nanoparticles in the field of catalysis, especially with regard to organic and/or specific catalysis.

In the present work, TiO_2 nanoparticles were synthesized and had their surface modified with gold nanoparticles in order to obtain a nanomaterial with high catalytic activity, which was measured in benzyl alcohol oxidation tests, as described in this manuscript.

2. Experimental

2.1 TiO_2 nanoparticles synthesis

Titanium oxide nanoparticles were synthesized by the hydrothermal method through the hydrolysis of titanium peroxocomplex gel. This gel was synthesized by the reaction between titanium isopropoxide IV ($Ti[OCH(CH_3)_2]_4$) and a solution of hydrogen peroxide (H_2O_2) 30% by volume, in a molar ration of 1:10 Ti:H_2O_2, with the volume adjusted to 100 mL using deionized water and the solution refluxed at 80 °C for 15 minutes, obtaining a yellow gel. A 10 g aliquot of this gel was added to 45 mL of deionized water and placed in the aluminum hydrothermal reaction, containing an internal Teflon beaker, placed in an oven at 140 °C for 24 hours. After this period, the solution was oven dried, obtaining a pale powder.

2.2 TiO_2 nanoparticle surface modification with Au nanoparticles

Gold dopped TiO_2 nanoparticles were obtained from the surface modification of TiO_2 nanoparticles with gold nanoparticles. Therefore, the reduction of gold in the presence of metal oxide nanoparticles was performed by the adapted Turkevich method (Gorup *et al.*, 2011). In a beaker, 98 mL of deionized water and 0.1 g of TiO_2 nanoparticles were added, heated under magnetic stirring to a temperature of 90 °C. Then, 1.0 mL of $HAuCl_4$ solution (0.1 mol L^{-1}) and 1.0 mL of sodium citrate solution (0.3 mol L^{-1}) were added. The mixture was kept under stirring and at a controlled temperature of 90 °C for 10 minutes. The solution was cooled to room temperature and the product was centrifuged and washed with deionized water and then dried in an oven.

2.3 Benzyl alcohol oxidation tests

To test the catalytic potential of the nanomaterials, catalytic tests were carried out in the oxidation reaction of benzyl alcohol in its derivatives in the presence of nanoparticles. One mL of benzyl alcohol was added with 0.3 g of potassium carbonate in the aluminum reactor with 0.005 g of TiO_2/Au nanoparticles which was closed and left for 24 h at 160 °C in the oven. For comparison, the same test was performed under the same conditions using TiO_2 nanoparticles and no catalyst.

2.4 Characterizations

Titanium oxide nanoparticles and gold doped titanium oxide nanoparticles were characterized by X-ray diffraction (XRD), UV-visible spectroscopy and infrared spectroscopy (UV-Vis). All nanoparticles' catalytic activity was investigated in the benzyl alcohol oxidation reaction and followed by infrared spectroscopy and gas chromatography coupled to mass spectrometer (GC-MS).

3. Results

It was possible to perform the synthesis of TiO_2 nanoparticles by the proposed method. X-ray analysis is shown in Fig. 1. The anatase peaks found at 2θ values of 25.28, 36.94, 48.04, 53.89, 55.06, 62.11, 68.76 and 70.30 correspond to the crystallographic planes (101), (103), (200), (105), (211), (213), (116) and (220), respectively. Rutile peaks appear at 2θ values of 27.44, 36.08, 41.22, 44.05, 62.74, 74.40 and 76.50 correspond to the crystallographic planes (110), (101), (111), (210), (002), (320) and (202), respectively. It was determined that the nanostructures had 71% of the anatase crystallographic phase (PDF 00-021-1272) and 29% of the rutile crystallographic phase (PDF 00-021-1276). The crystallite size measured by Scherrer equation was 15 and 27 nm for rutile phase (110 and 310) showing rod shape particles and 9 nm for anatase phase shown spherical shape (101 and 200).

Recently, TiO_2 nanomaterials have been prepared by different methodologies, where liquid phase processing stands out. The characteristics of the material are closely linked to the synthesis methodology (S. Gupta and Tripathi, 2011). It is verified in the literature the possibility of obtaining nanomaterials with different size, morphology and crystallographic phase, as it has been reported the obtention of 60 nm size TiO_2-anatase nanoparticles (J. Zhang *et al.*, 2017), 5.7 nm sized nanorods (Dalod *et al.*, 2017) and even TiO_2-rutile nanotubes sizing 20 nm in diameter (Yan *et al.*, 2010).

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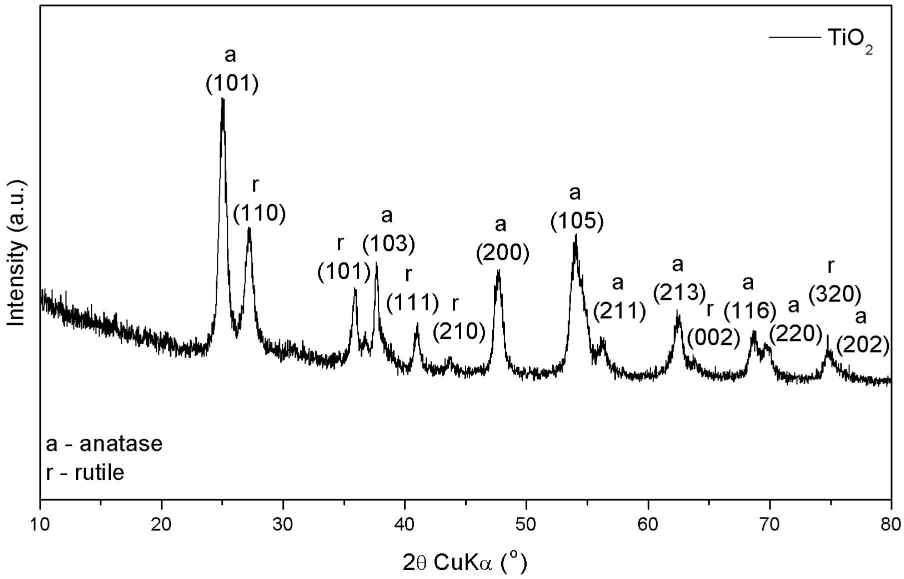

Figure 1. TiO_2 nanoparticles XRD patterns.

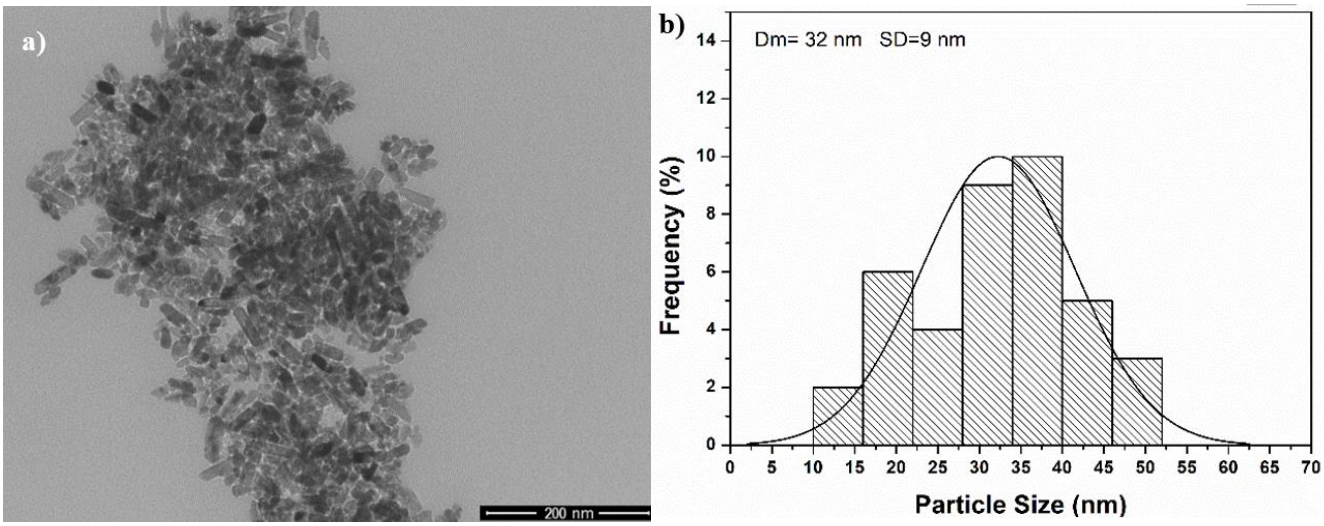

Figure 2. TEM images **(a)** and size distribution histogram **(b)** for TiO_2 nanoparticles.

Transmission electron microscopy (TEM) images were able to confirm the average size 32 nm at length and show rod shape morphology, as seen in the Fig. 2. Figure 3 shows a scanning electron microscopy (SEM) image of the TiO_2 nanoparticles, which shows a uniform distribution of the nanomaterial.

TiO_2 nanoparticles modified with gold (TiO_2/Au) were also analyzed by XRD, whose diffractogram is shown in Fig. 4. The presence of Au nanoparticles on the surface of TiO_2 nanoparticles is confirmed by the presence of peaks found at 2θ values of 32.19 and 46.12, corresponding to the crystallographic planes (111) and (200) (Beck *et al.*, 2008; C. Zhao *et al.*, 2006).

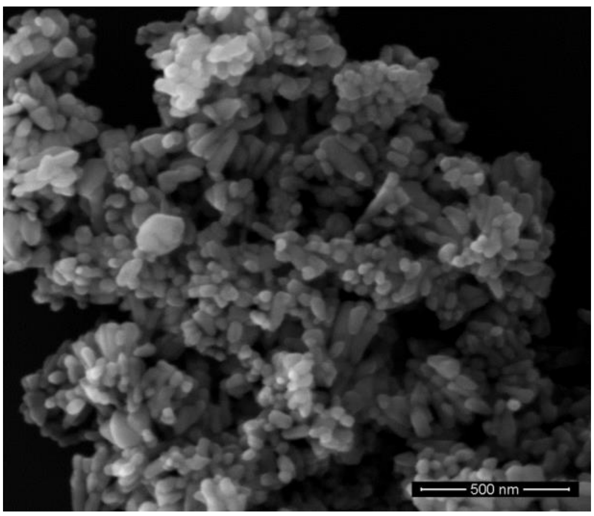

Figure 3. SEM image of TiO_2 nanoparticles.

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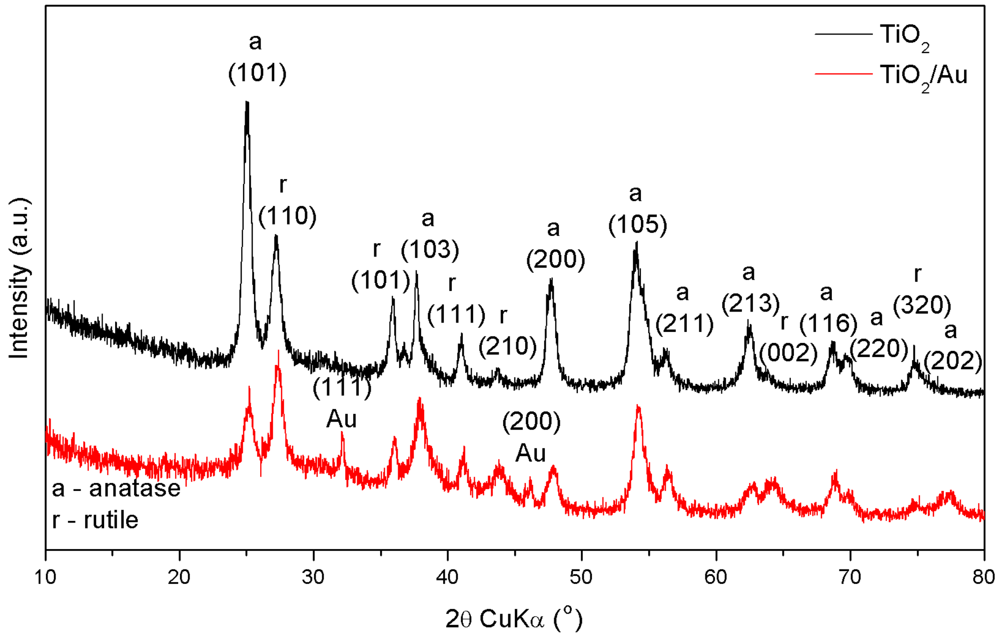

Figure 4. TiO_2/Au nanoparticles XRD patterns.

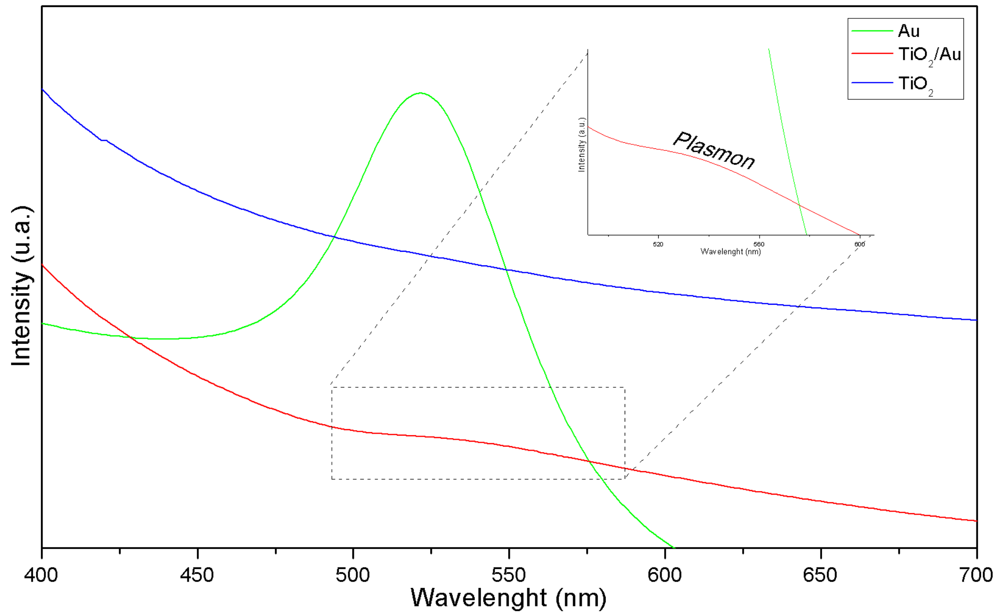

Figure 5. TiO_2/Au, TiO_2 and Au nanoparticles UV-Vis spectra.

The presence of gold nanoparticles coating the surface of titanium oxide nanoparticles was also verified by UV-Vis spectroscopy showing the Au nanoparticles the plasmon band at 550 nm. The presence of the plasmon band characteristic of gold in TiO_2/Au nanoparticles contributes to the characterization of the material (Verma *et al.*, 2020). This band formation can be seen in Fig. 5.

Figure 6 shows FEG-SEM images of TiO_2/Au nanoparticles. Although it is possible to observe the TiO_2 nanoparticles, the spherical gold nanoparticles are not visible. It is believed that this was due to image resolution or even the low concentration or size of the nanoparticles. However, it is noteworthy that the other characterization techniques proved their presence.

TiO_2 nanoparticles were shown to be active for catalyzing the oxidation of benzyl alcohol, showing significant yield, even more so for titanium oxide nanoparticles coated with gold nanoparticles. Uncoated TiO_2 nanoparticles showed a catalytic yield of 1.4% and gold dopped TiO_2 nanoparticles showed a catalytic yield of 73% and this catalyst showed to be selective (> 98%),

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converting benzyl alcohol only to benzaldehyde. Figure 7 shows the chromatogram of the tests' product. An analysis of the precursor was also carried out under the same conditions to identify and determine the level of purity of the alcohol, since it is naturally oxidized by air over time.

In addition, the mass spectrum of the species was also analyzed. Figure 8a shows the mass spectra of benzyl alcohol, as well as its characteristic fragmentation, showing peaks in m/z 108, 107, 91, 79, 77 and 51, which, according to the literature and the equipment's database, characterize the benzyl alcohol. Figure 8b shows the mass spectrum and characteristic fragmentation of benzaldehyde, the peaks at m/z 106, 105, 77, 51 and 50 are also in accordance with the literature and characterize benzaldehyde. Figure 8c shows the mass spectrum and characteristic fragmentation of benzyl benzoate, whose peaks at 212, 105, 91 and 77 characterize benzyl benzoate.

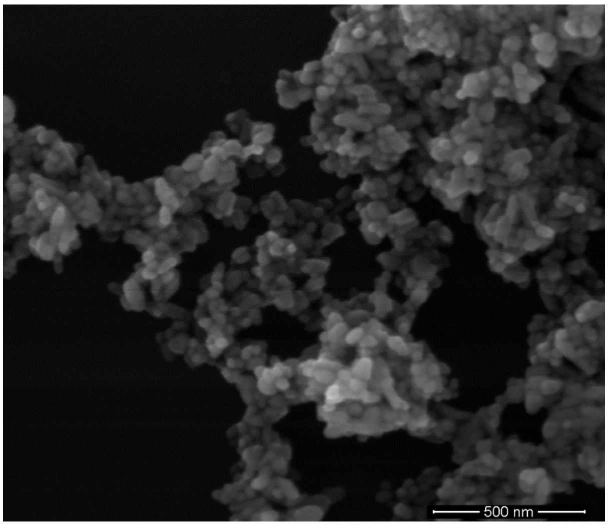


Figure 6. FEG-SEM image of TiO_2/Au nanoparticles.

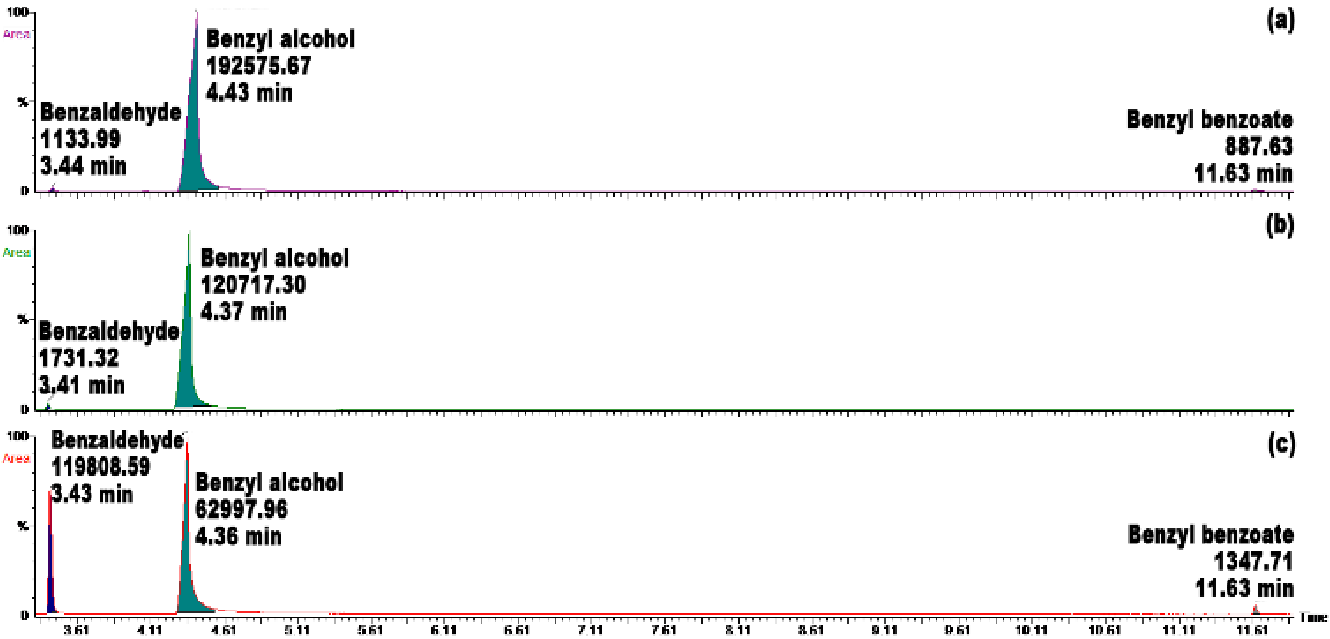
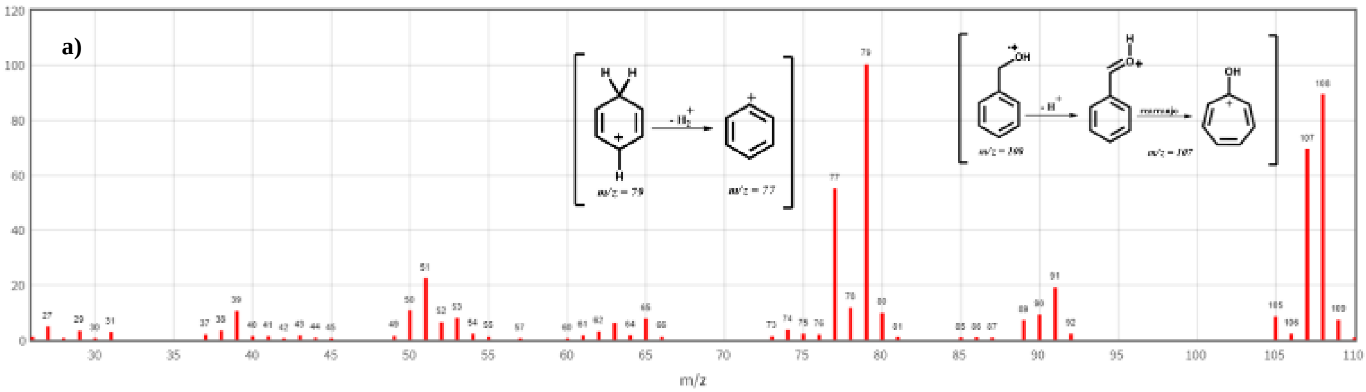


Figure 7. Chromatogram of **(a)** benzyl alcohol, **(b)** TiO_2 NPs catalyzed product and **(c)** TiO_2/Au NPs catalyzed product.



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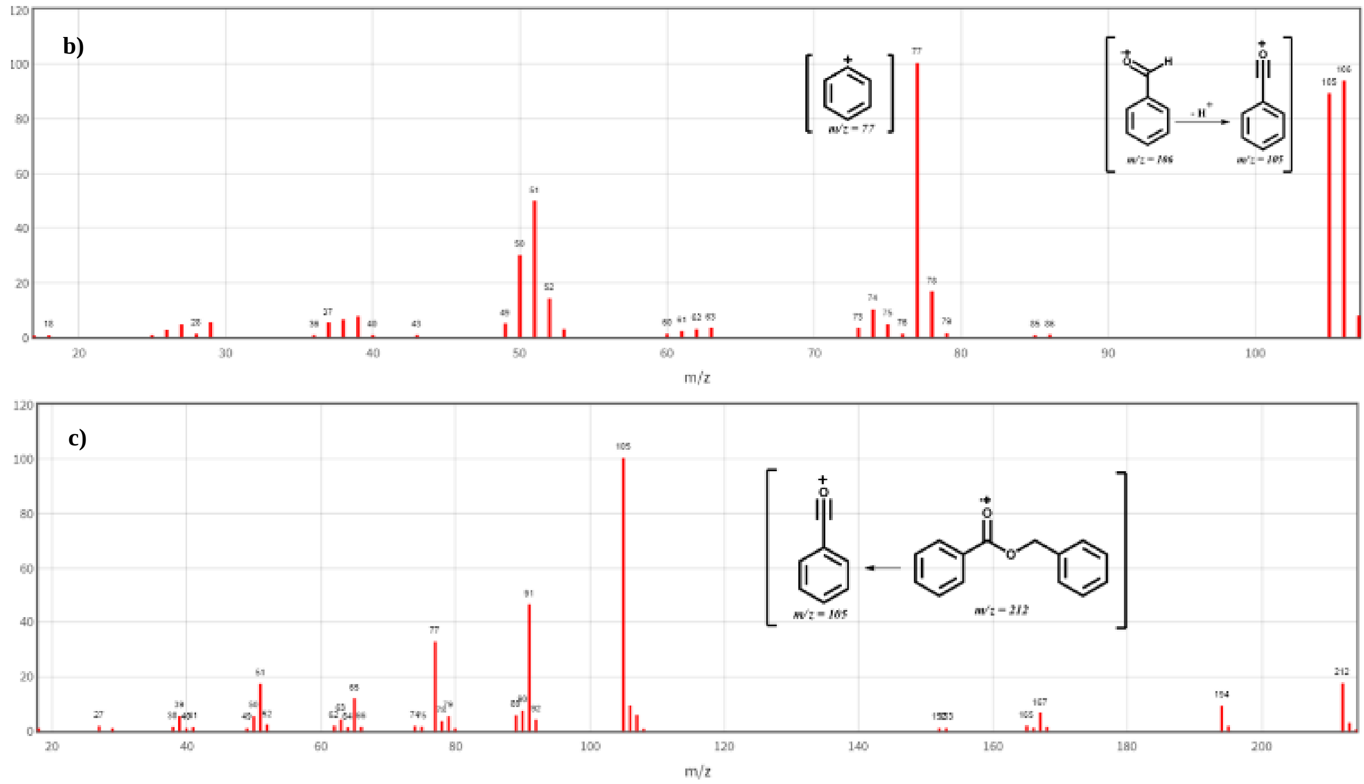

Figure 8. Mass spectra and characteristic fragmentations: **(a)** Benzyl alcohol; **(b)** Benzaldehyde and **(c)** Benzyl benzoate.

Figure 9 shows the Fourier transform infrared spectroscopy (FTIR) spectra of the tests' products, where the appearance of a characteristic band by the C=O stretch can be noticed, which also shows the formation of benzaldehyde.

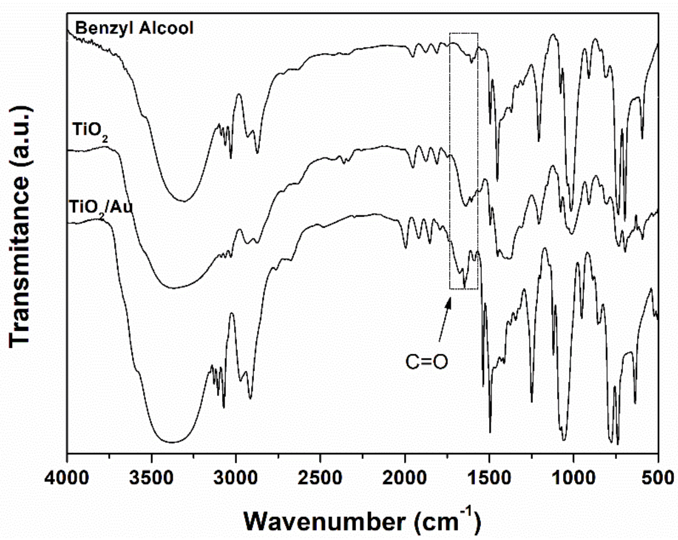

Figure 9. FTIR spectra for TiO_2/Au NPs, TiO_2 NPs oxidated product and pure benzyl alcohol.

The Gas chromatography–mass spectrometry (CG-MS) and FTIR spectra showed that the nanoparticles showed selectivity, where only the presence of benzaldehyde was observed as a reaction product. Selective oxidation of alcohols is one of the most significant transformations of organic chemistry since it is essential for industrial intermediates production, such as ketones, epoxides, aldehydes and acids. Previous reports (Conte *et al.*, 2010; Fristrup *et al.*, 2008), that supported that Au nanoparticles catalyze the oxidation of benzaldehyde by enhancing the formation of the intermediate acyl radicals, rule out the possibility that the supported gold–palladium catalyst used in our earlier work on benzyl alcohol oxidation is responsible for the inhibition of benzaldehyde oxidation. The only other component, which could prevent the further oxidation of benzaldehyde, is the remaining benzyl alcohol. In recent study, Sankar *et al.* (2014) demonstrate by chromatographic analyses of reaction mixtures during the initial stages of oxidation of benzyl alcohol; the analysis revealed that no other products were formed and confirm Partenheimer's observations that in benzyl alcohol oxidation catalyzed by Co (III), benzoic acid production only begins to accelerate when the benzyl alcohol level in the reaction mixture falls below ~10%. That a very small amount of benzyl alcohol, present in benzaldehyde, is evidently involved in preventing the oxidation of benzaldehyde to benzoic

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acid forms the premise for the more detailed studies presented below. The authors showed that benzyl alcohol was probably acting to quench free radicals involved in autoxidation of benzaldehyde and that related molecules should act similarly.

Comparing with other authors giving in Tab. 1, it is noted that TiO_2 nanoparticles are used for developing several nanostructured catalysts, mainly using them with noble metals. The nanomaterial synthesized in this work presented a conversion rate and selectivity superior to other works.

Table 1. Catalytic performance of nanoparticles in benzyl alcohol oxidation.

Type	Catalyst	Conversion (%)	Selectivity[a] (%)	Reference
Catalysis	Pd/TiO_2	4.5	85.9	Sun *et al.* (2017)
	$Au@Pd/TiO_2$	14.3	91.6	
	Au/TiO_2 nanotube	23.2	> 99.0	Verma *et al.* (2020)
	Au/TiO_2 nanorod	32.5	> 99.0	
	Au/TiO_2 microporous	9.6	> 99.0	
	Pd/TiO_2	57.6	74.1	Weerachawanasak *et al.* (2015)
	Pt/TiO_2 (anatase)	76.7	> 99.0	Liu *et al.* (2017)
	Pt/TiO_2 (rutile)	34.3	> 99.0	
	TiO_2	1.6	79.3	Du *et al.* (2020)
	Pd/TiO_2	39.1	70.3	
	TiO_2	3.0	88.0	Nowicka *et al.* (2019)
	$Pd/Zn/TiO_2$	52.0	67.0	
Photocatalysis	TiO_2	3.4	> 98.0	X.-F. Zhang *et al.* (2019)
	Au/TiO_2	16.3	> 98.0	
	Pt/TiO_2	32.2	> 98.0	

[a] Selectivity to benzaldehyde.

4. Conclusions

We presented herein the synthesis of a heterogeneous catalyst comprised of TiO_2 and TiO_2/Au NPs, with a controlled rod shape morphology and average size 32 nm. The catalyst exhibited remarkable and efficient activity for the benzyl alcohol oxidation. The CG-MS and FTIR spectra showed that the nanoparticles showed selectivity, where only the presence of benzaldehyde was observed as a reaction product. This work provides great potential for the selective oxidation of alcohols with high activity.

Authors' contribution

Conceptualization: Gabriel, A. M.; Malaquias, K. S.; Cristovan, F. H.; Arantes, T. M.
Data curation: Gabriel, A. M.; Malaquias, K. S.
Formal Analysis: Gabriel, A. M.; Malaquias, K. S.; Arantes, T. M.
Funding acquisition: Arantes, T. M.
Investigation: Gabriel, A. M.; Malaquias, K. S.; Cristovan, F. H.; Arantes, T. M.
Methodology: Gabriel, A. M.; Malaquias, K. S.; Cristovan, F. H.; Arantes, T. M.
Project administration: Cristovan, F. H.; Arantes, T. M.
Resources: Malaquias, K. S.; Cristovan, F. H.; Arantes, T. M.
Software: Not applicable.
Supervision: Arantes, T. M.
Validation: Malaquias, K. S.; Cristovan, F. H.; Arantes, T. M.
Visualization: Gabriel, A. M.; Arantes, T. M.
Writing – original draft: Gabriel, A. M.
Writing – review & editing: Gabriel, A. M.; Cristovan, F. H.; Arantes, T. M.

Data availability statement

All data sets were generated or analyzed in the current study.

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