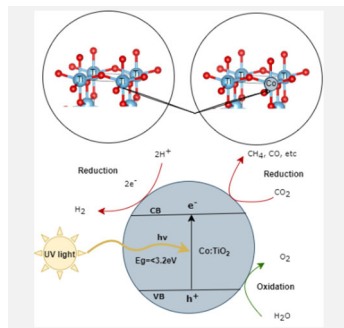


OBTAINING SHORT CHAIN HYDROCARBONS THROUGH PHOTOCATALYTIC CO₂ REDUCTION USING COBALT DOPPED TiO₂

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Titanium oxide (TiO₂) was produced via the sol-gel method, incorporating cobalt. The cobalt content was varied at 1%, 3%, 5%, and 10% mol. The resulting materials underwent comprehensive characterization using a range of techniques: XRD, FTIR, XPS, UV-vis, photoluminescence, nitrogen physisorption, SEM-EDS, HRTEM. The photocatalytic activity was evaluated by means of hydrocarbons produced quantity. The detailed analysis revealed successful doping of the material, also to the formation of the anatase-brookite phase. Among the array of catalysts evaluated, the 1%Co:TiO₂ catalyst emerged as the most efficient, yielding notable quantities of methane (15 mmol/h) and ethane (0.5 mmol/h).

Introduction

Atmospheric pollution has increased due to the different antropogenic activities, being CO₂ the gas with the highest presence and the main cause of the greenhouse effect.

In recent years, the way to reduce this gas has been studied, using artificial photosynthesis [1] or also known as photocatalytic reduction; in this process it is necessary a photocatalyst that allows to absorb energy and promote the excitation of electrons in the valence band to the conduction band leaving holes (e⁻/h⁺), causing the reduction of CO₂ and the oxidation of pollutants in water.

The most widely used semiconductor is titanium dioxide (TiO₂) because it has high photoactivity, chemical stability, low cost and is non-toxic in nature; however, it has disadvantages such as rapid recombination of charge carriers and it works under ultraviolet light. According to the literature review, it was observed that TiO₂ showed better results when doped with transition metals [2], obtaining products such as CH₄, CO and C₂H₆.

Material and Methods

The sol-gel method was chosen to synthesize cobalt-doped TiO₂ photocatalysts with varying concentrations (1%, 3%, 5% and 10% mol). All materials underwent calcination at 400°C and were subjected to thorough characterization using a variety of techniques, including XRD, FTIR, UV-vis, photoluminescence, nitrogen physisorption, SEM-EDS, HRTEM, and photocatalytic activity assessment.

For the CO₂ reduction tests, a glass reactor with 200 mL of the working solution, composed of methanol and distilled water type II was used. A UV Pen-Ray Lamps model 90-0012-01 mercury lamp served as the light source. The photocatalytic reaction spanned a duration of 6 hours, with samples withdrawn and subjected to analysis every hour. The analysis itself

was conducted using a SHIMADZU GC-2014 gas chromatograph equipped with Flame Ionization Detector (FDI) and Thermal Conductivity Detector (TCD).

Results and Discussion

Figure 1 depicts the X-ray diffraction patterns of the synthesized titanium oxide, discernible diffraction lines the anatase phase was observed in according with PDF 00-021-1272. However, upon meticulous refinement analysis, it became evident that a mixture of phases was present, with a minor fraction attributed to the brookite phase (21-17%) PDF 00-029-1360.

The results obtained suggest a noteworthy relationship between the increase in cobalt content and a concurrent decrease in crystal size (Table 1). This observation implies that the introduction of cobalt exerts a discernible influence on the crystalline structure, thereby impacting the phase composition and overall characteristics of the synthesized titanium oxide materials.

In Figure 2, the FTIR spectra of the samples are presented within the 4000-400 cm⁻¹ range. Notably, a broad band is evident at a wavelength of 3250 cm⁻¹, attributed to the O-H bond. Additionally, a distinct band is observed at 1653 cm⁻¹, signifying Ti-O-H stretching bonds associated with hydroxyl groups or H₂O[3]. This presence of water-related bonds is attributed to the humidity within the samples, where water molecules are adsorbed on the porous surface of the material.

The synthesized samples were subjected to UV-vis spectroscopy analysis, which revealed a shift towards the visible light region (380-750 nm). Using the F(R) Kubelka-Munk function and the Tauc method to determine the forbidden energy band of the materials (TiO₂ an indirect band gap semiconductor [4]), revealed remarkable changes in the optical properties.

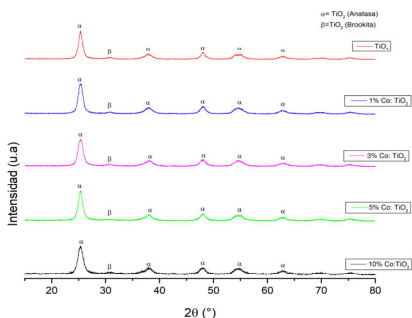


Figure 1. Diffraction patterns for TiO₂, 1% Co: TiO₂, 3% Co: TiO₂, 5% Co: TiO₂ and 10% Co: TiO₂.

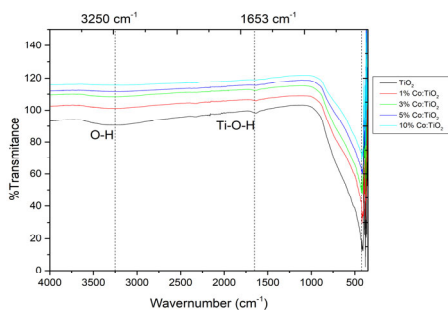


Figure 2. FTIR spectra of the samples

In particular, the values obtained for cobalt-doped TiO₂ showed a reduction (Table 1) compared to the 3.2 eV band indicated in the literature. This reduction

Table 1. Comparison of different properties

Sample	Band gap (eV)	%Anatasa	% Brookita	Crystal size (nm)	
				Anatasa	Brookita
TiO ₂	3.13	78.29	21.71	11.94	9.0
1%Co: TiO ₂	3.02	81.17	18.83	10.46	8.6
3%Co: TiO ₂	2.85	80.08	19.92	9.53	8.0
5%Co: TiO ₂	2.68	82.44	17.56	10.6	7.0
10%Co: TiO ₂	1.8	79.31	20.69	9.3	6.9

Conclusions

Incorporating cobalt ions into the TiO₂ photocatalyst via the sol-gel method resulted in notable modifications in crystal size, phase composition and the forbidden band energy. This alteration indicates a significant impact of cobalt doping on the electronic structure and optical properties of the photocatalyst.

In terms of catalytic activity, all samples demonstrated methane production, suggesting a commonality in CO₂ reduction capability. However, ethane production was observed exclusively in photocatalysts doped with cobalt at concentrations below 5 mol%. Remarkably, the photocatalyst with 1 mol% cobalt exhibited superior performance, manifesting as the most efficient catalyst among those tested. This finding underscores the importance of cobalt doping concentration in influencing the selectivity and efficiency of hydrocarbon product formation during CO₂ reduction.

References

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means a lower energy requirement to excite electrons from the valence band to the conduction band, indicating the impact of cobalt doping in altering the optical characteristics of the material.

Based on the experiments conducted, it was determined that the photocatalyst containing 1% mol of cobalt (Figure 3) exhibited the highest efficiency. Interestingly, all photocatalysts generated methane as a product of the CO₂ reduction process. However, it was observed that only two of the photocatalysts were capable of producing ethane as a byproduct. This finding suggests that while cobalt doping enhances the production of high-value products during CO₂ reduction, the concentration of cobalt may also play a crucial role in influencing the selectivity of the products generated.

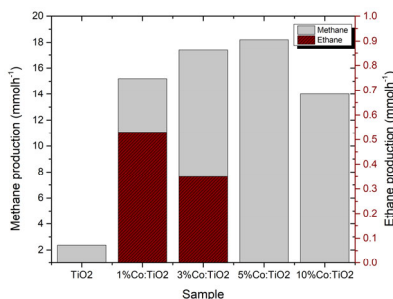


Figure 3. Catalytic activity for the reduction of CO₂