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THE DEGRADATION OF METHYLENE BLUE OVER M_2TiO_4 SPINEL PHOTOCATALYST

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Résumé

La photocatalyse hétérogène est un processus d'oxydation avancée (POA). Elle a été largement étudiée par de nombreux chercheurs dans le monde. Cette technique est utilisée pour dégrader ou éliminer un large éventail de polluants dans l'eau et de l'air. Dans cette étude, l'oxydation photocatalytique et la minéralisation de bleu de méthylène dans une suspension aqueuse contenant du cobalt titanate préparé par coprécipitation a été utilisé comme photocatalyseur dans un réacteur hélicoïdal. La photodégradation a été étudiée au moyen de deux types de lampes à une irradiation émettant à 254 nm et l'autre émettant à 365 nm. Les résultats ont montré que la photodégradation est une méthode efficace pour l'élimination du bleu de méthylène. L'efficacité du procédé dépend fortement des conditions expérimentales de synthèse. Nous avons observé que 40 % du polluant a été dégradé après 3 heures d'irradiation UV.

Mots clés : Photocatalyse, coprécipitation, POA, cobalt titanate, bleu de méthylène, caractérisation.

Abstract

Heterogeneous photocatalysis is an advanced oxidation process (AOP) which has been widely studied by numerous researchers in the world and is used to degrade or remove a wide range of pollutants in water and air. In this study, the photocatalytic oxidation and mineralization of methylene blue in aqueous catalyst suspensions of coprecipitated cobalt titanium oxide has been carried out in a helical reactor. The photodegradation was investigated using two kinds of irradiation lamps one emitting at 254 nm and the other emitting at 365 nm. Results showed that photodegradation is an effective method for the removal of MB from wastewaters. The efficiency of the process depends strongly on the experimental conditions of synthesis. We observed that 40 % of pollutant was degraded after 3 hours of UV irradiation.

Keywords: Photocatalysis, Coprecipitation, AOP, cobalt titanium oxide, methylene blue, Characterization.

ملخص.

التحفيز الضوئي غير متجانس هي عملية أكسدة متقدمة التي تمت دراستها على نطاق واسع من قبل العديد من الباحثين في العالم، ويستخدم لتتحلل أو إزالة مجموعة واسعة من الملوثات في الماء والهواء. في هذه الدراسة، وقد تم تنفيذ أكسدة تمعدن الأزرق الميثيلين في تعليق حافزا مائي من ترسب الكوبالت أكسيد التيتانيوم في مفاعل حلزونية. وكان التحقيق في التحلل الضوئي باستخدام نوعين من أشعة المصابيح الباعثة للواحد في 254 نانومتر، والآخر في انبعاث 365 نانومتر. وأظهرت النتائج أن التحلل الضوئي هو وسيلة فعالة لإزالة الأزرق الميثيلين من مياه الصرف الصحي. كفاءة العملية تعتمد بقوة على الظروف التجريبية. لاحظنا أن 40٪ من الملوثات يتحلل بعد 3 ساعات من الأشعة فوق البنفسجية.

الكلمات المفتاحية: تحفيز ضوئيا لكوبالت أكسيد التيتانيوم ، الأزرق الميثيلين، الخصخصة

Introduction :

The elimination of toxic chemicals from wastewater is presently of great concern, because their complete biodegradation requires several days or weeks. Toxic organic compounds must be removed to an acceptable level before discharged to receiving waters. Recently, it has been demonstrated that semi-conducting materials mediating photocatalytic oxidation of organic compounds can be an alternative to conventional methods for the removal of organic pollutants in water and air [1].

It is well known that when a semiconductor absorbs a photon with energy greater than or equal to band gap energy, an electron would be promoted from the valence band to the conduction band, leaving a hole in the valence band. If this charge separation is valid, these induced electrons and holes can be used for efficient photocatalytic degradation for organic pollutants [2]. Holes can react with the surface–bound H_2O or OH^- to generate a powerful oxidant such as hydroxyl radicals, and the conduction band electron may be picked up by the dissolved oxygen species to form superoxide anion radicals [3]. These active radicals will oxidize the organic pollutants.

Titanium (IV) oxide suspended in water has been proven to be one of the most active photocatalyst. However, it has been shown that the photocatalytic activity of TiO_2 is limited by fast charge–carrier recombination and low interfacial charge-transfer rates of photogenerated carriers [4]. Therefore, the search for novel materials in heterogeneous photocatalysis with high performance has been a matter of interest in the last years.

Keeping the mentioned discussion in the mind, the present study aims at (a) the synthesis of material at nanoscale by coprecipitation method, (b) to test the adsorption characteristics of the synthesized material using methylene blue as adsorbate.

2-EXPERIMENTAL

2- 1- Preparation of materials

The photocatalysts nanoparticles were obtained by coprecipitation method. Titanium chloride ($TiCl_4$) and cobalt chloride hexahydrate ($CoCl_2.6H_2O$, biochem chemopharma) were used as starting materials. Potassium hydroxide solution (KOH, Prolabo) was used as precipitant agent without further purification. The corresponding precursors in 2:1 molar ratio was dissolved in 200 ml of deionized water. Then, KOH was added dropwise to adjust pH to about 10 under vigorous stirring. The reaction mixture was aged at 80°C for 1 h. After purification process which implies washing with hot water and ethanol. The precursor was calcined at 600 and 900°C for 2h.

2-2- Characterization

Thermogravimetric measurements of the precursor was performed from ambient temperature to 800°C in flowing N_2 at a rate of 10°C min^{-1} on a TA instruments thermoanalyzer. Powder X-ray diffraction (XRD) patterns were recorded at ambient temperature on a Xpert-pro diffractometer using Cu K_α radiation (λ = 1.5406 Å) under the accelerating voltage of 45 kV in the 2θ = 5-90° range at a scanning rate of 5°/min. Specific surface area and porosity measurements were carried out on a Quantachrome Novawin2 instrument at liquid nitrogen temperature using nitrogen gas as adsorbate. Fourier Transformed Infrared spectra (FTIR) were recorded using the KBr pellet technique on a Shimadzu 8400 spectrometer in the 400-4000 cm^{-1} range. The Raman spectra of the samples were recorded on a Horiba Labram HR Evolution. Scanning electron microscopy observations (SEM) were performed by using a Zeiss Supra mke.

2-3- Photocatalytic test

The photodegradation of MB in aqueous solution was monitored in the presence of photocatalyst calcined at 600°C and 900°C. All the photocatalytic experiments were performed in the experimental installation shown in Figure 1. The helical photoreactor of 500 ml capacity was constructed in Pyrex. It is comprised of 23 spires with a 7 mm interior diameter and a length of 400 mm. The source of irradiation is placed in the center of the reactor to assure the maximum energy exchange between the source of irradiation and reaction mixture that flows out continuously. The tubular compartment surrounding the lamp has an interior and outer diameter equal to 60 and 80 mm, respectively, a length of 50 cm are used as a cooling system. A pump recirculates the mixture between the reactor and the reservoir.

The suspension was prepared by adding 100 mg of photocatalyst into 1 L of MB aqueous solution (30 mg L^{-1}). Before irradiation, the suspension was magnetically stirred in the dark for 60 min to establish the adsorption/desorption equilibrium at room temperature.

At regular intervals, samples were taken from the suspension and then centrifuged to remove the photocatalyst particles. The change in the concentration of each degraded solution was monitored on UV–vis spectrophotometer shimadzu by measuring the absorbance in 300-600 nm for MB. Distilled water was used as reference sample.

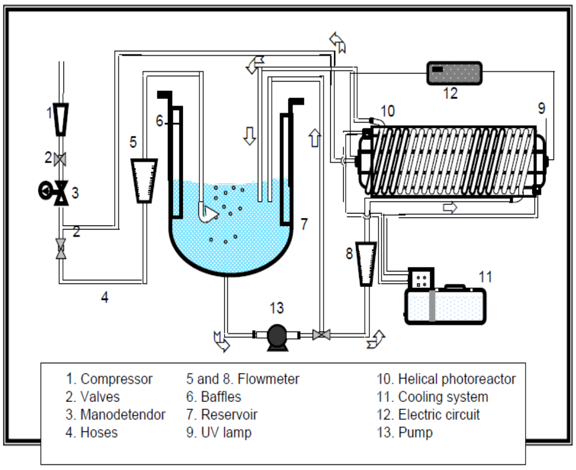


Fig.1. Experimental setup of the helical reactor [4].

3- RESULTS AND DISCUSSION

3-1- Structural characterization

X-ray diffraction pattern of photocatalyst calcined at 600°C and 900°C for 2h is shown in figure 2. XRD patterns are consistent with the well-crystallized solids. At 600°C, a mixture of TiO_2 (JCPDS 21-1272) and Co_3O_4 (JCPDS 42-1467) are obtained by the mean peaks located at 2θ = 25.41° and at 36.8°, 31.48, 37.18, 59.38, and 65.28, respectively. In contrast, the spinel Co_2TiO4 (PDF 39-1410) was the only phase present at 900 °C. These results explain the significant effect of calcination temperature in the formation of pure spinel Co_2TiO_4.

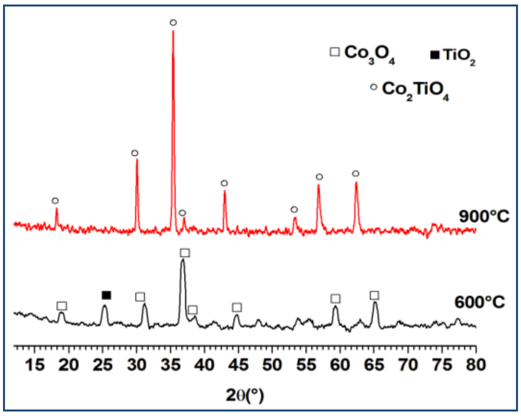
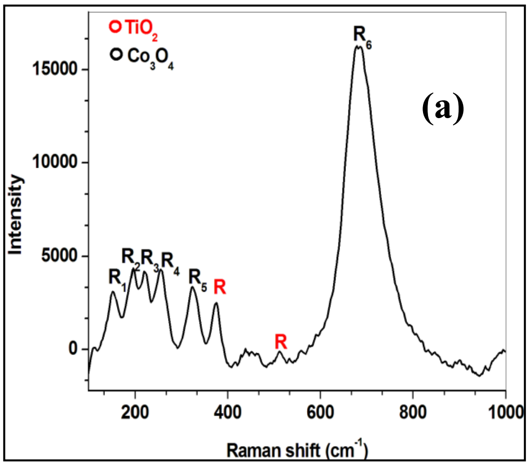


Fig.2. XRD pattern of the photocatalysts calcined at 600°C and 900°C.

The phases and the mean grain size of the photocatalysts were determined according to the XRD results. The mean grain size was estimated by applying the Scherrer's equation and selecting the crystal planes (3 1 1) and (1 1 0) for Co_2TiO_4 and TiO_2, respectively. The results are gathered in table 1. The quantification led to the value the spinel unit cell parameter (a = 8.431 Å) and of the crystallite size Cs = 42 nm for the sample treated at 900 °C. For the solid treated at low temperature (mixed oxides in their structure), anatase phase presents a smaller crystallite size compared with Co_3O_4 (29 nm for TiO_2 against 36 nm for Co_3O_4) (Table 1).

Laser Raman spectra of the sample calcined at 600 and 900 °Care shown inFigure3. The sample treated at 600 °C (Figure 3-a) showed that ttitanium oxide is characterized by three bands, located at 397, 514, and 640 cm^{-1}.The bands at 397 and 640 cm^{-1} are assigned to B1g andE1g modes, respectively, while the band at 640 cm^{-1} is a doublet of A2g and B1g modes. TiO_2 with 10% in the phase Co_3O_4-TiO_2 gives rise to a new absorption near 679 cm^{-1} and two shoulders, at 446 and 512 cm^{-1}, assigned to the A1g, Eg, and F2g active Raman modes of the spinel Co_3O_4, respectively[5].

The Raman spectrum of the spinel phase Co_2TiO_4 (Figure 3-b) showed six peak maxima at 355, 434, 455, 525, 624 and 795 cm^{-1} characterized the presence of Co_2TiO_4 phase. This result is in good agreement with those observed by XRD analysis.



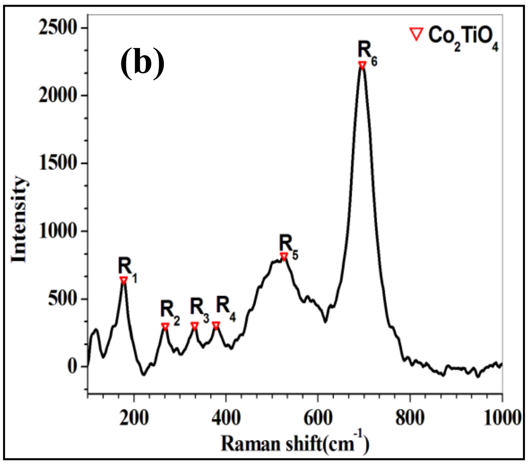


Fig.3. Raman spectra of photocatalyst calcined at 600 (a) and 900°C (b).

FTIR results (Figure 4) showed for the sample calcined at 600 °C two strong absorption bands at 661 and 564 cm^{-1} (Figure 4-a) which is an indication of the formation of Co_3O_4 with a spinel structure [6]. The general feature, which follows from the group-theoretical treatment i.e. the number of infrared active modes is limited to four, is still valid for the titanate spinels. For the catalyst treated at 900 °C, FTIR spectra (Figure 4-b) shows in the measured range three absorptions; in addition to this triplet. Another absorption was reported by Preudhomme [7] below 200 cm^{-1} for Co_2TiO_4, which completes the number to four. These absorption bands are rather broad compared with those reported in literature for normal spinels. This is in agreement with the fact that Ti^{4+} ions have a strong preference for the octahedral environment, which means that Co_2TiO_4 titanate spinel is mainly inverse [8].

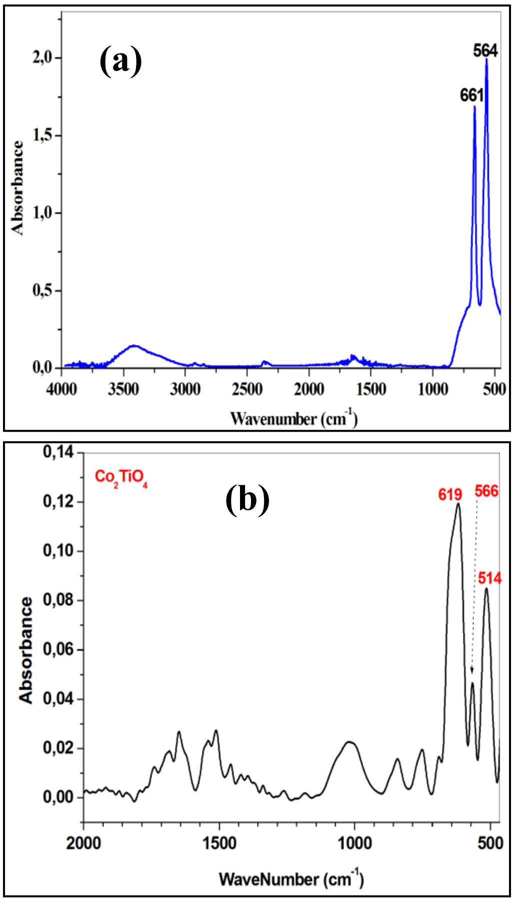


Fig.4. FTIR spectra of photocatalystcalcined at 600 (a) and 900 °C (b).

3-2-Textural characterization

The specific surface areas (S_{BET}) are gathered in Table 1. It largely depends on the calcination temperature. When the calcination temperature increase of 600 to 900 °C, the specific surface areas decrease 57 to 10 (m^2/g).The low S_{BET} of CP-900 catalyst could be attributed to the presence of another oxide in very small amount (can not be detected by XRD analysis) beside spinel structure assuming that they are deposited on the spinel surface blocking some pores.

The morphology of catalysts was studied by SEM analysis. The obtained results are showed in figure 5. The shape and the surface morphology of CP-900 sample (Figure 5-b) as seen from SEM consist of well-crystallized grains with uniform distribution and highest grain size was observed, in accordance with it's low specific surface area. In contrast, CP-600 catalyst, a mixture of size was observed suggesting that the presence of binary system. This is in good agreement with XRD and Raman analysis.

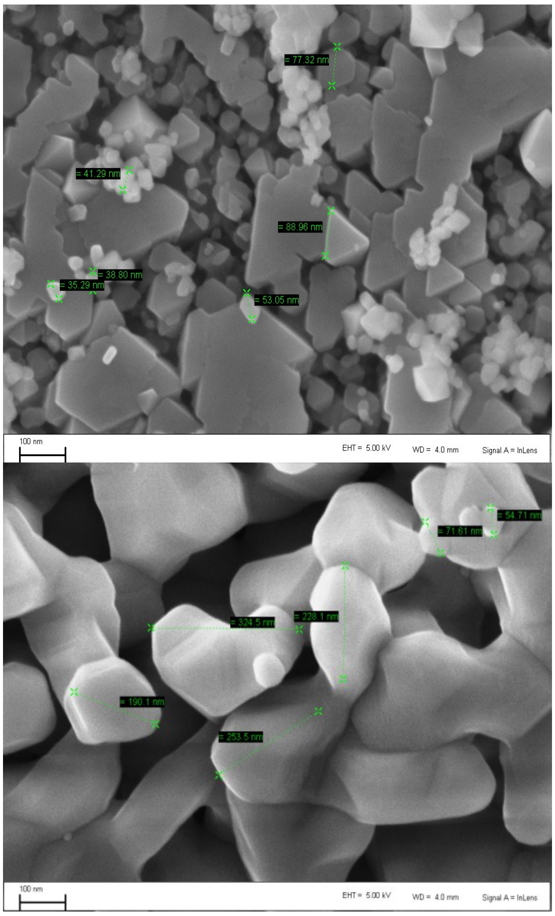


Fig.5. SEM observations of the photocatalyst calcined at 600 (a) and 900°C (b)

3-3-Photocatalytic activity:

To investigate the catalytic activity of orthotitanate for UV degradation of methylene blue (MB), series of experiments were carried out. As shown in Figure 6, the concentration of MB did not obviously decrease in the presence of both catalysts when the suspension was irradiated with UV radiation at wavelength λ = 365 nm. With this first experiment (UV (λ=356 nm) / photocatalysts) we obtained approximatively 5 % of degradation.

Catalysts	phase	S_{BET} (m^2/g)	Cs (nm) XRD	Lattice parameter (Å)
CP 600°C	TiO_2	57	29	a=b= 4.975; c= 2.95
	Co_2O_3		36	8.088
CP 900°C	Co_2TiO_4	10	42	8.431

Table 1. The phase, crystallites grain sizes and surface BET of coprecipited samples at different calcinations temperatures.

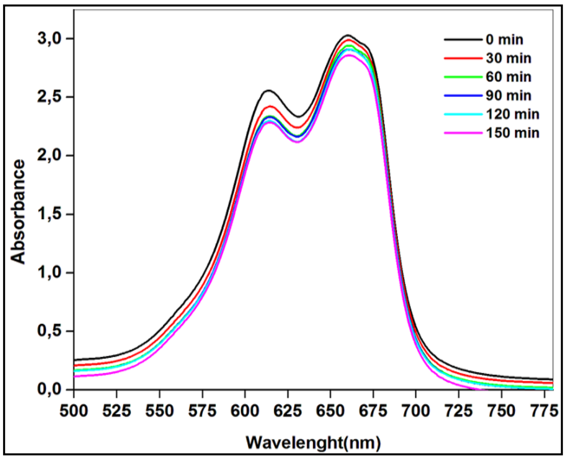


Fig.6. Photocatalytic activity of photocatalyst under UV light (λ=365 nm).

However, compared to the system UV (λ=356 nm)/ photocatalyst, the UV (λ=254 nm) / photocatalyst system showed more effective in the degradation of methylene blue.

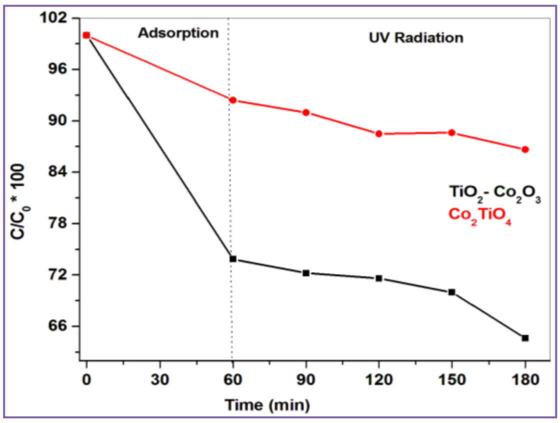


Fig.7. Photocatalytic activity of photocatalysts under UV light (λ=254 nm).

The decolorization rate (η) is 15% for cobalt orthotitanate Co_2TiO_4, which can be calculated with the formula [$\eta=(A_o-A)/A_o\times100\%$], where A_o and A stand for the absorbency of the undecomposed and decomposed solution, respectively.

The phase mixture TiO_2-Co_2O_3 exhibits a better activity toward the degradation of methylene blue; we can reach 40% of degradation after 180 min with UV light emitting at 254 nm.

CONCLUSION

Photocatalyst nanomaterials based cobalt titanium oxides have been prepared by coprecipitation technique. It led to the formation of a pure Co_2TiO_4 crystalline spinel phase at 900 °C. Their photocatalytic activity depended strongly on the calcinations conditions. The phase mixture TiO_2-Co_2O_3 exhibits a better activity toward the degradation of methylene blue; we can reach 40% of degradation after 180 min with UV light emitting at 254 nm.

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REFERENCES

[1]. B. Ismail, S. T. Hussain, S. Akram, Chemical Engineering Journal 219 (2013) 395–402.

[2]. Characterization of Semiconductor Heterostructures and Nanostructures. Carlo Lamberti (editor), ELSEVIER, 2008.

[3]. S.N. Basahel, I.H. Abd El-Maksod, B.M. Abu-Zied, M. Mokhtar, Journal of Alloys and Compounds 493 (2010) 630-635.

[4]. N.A. Laoufi, D. Tassalit, F. Bentahar, Global NEST Journal 10 (2008) 404-418.

[5]. Y. Brik, M. Kacimi, M. Ziad, F. Bozon- Verduraz, Journal of catalysis 202 (2001) 118-128.

[6]. J. Popović, E. Tkalčec, B. Gržeta, S. Kurajila, B. Rakvin, American Mineralogist 94 (2009) 771-776.

[7]. R. A. Nyquist, C.L. Putzig, M. A. Leugers « Hand Book of Infrared and Raman spectra of inorganic compounds and organic salt », Academic Press, 1997.

[8]. J. Preudhomme, P. Tarte, Spectrochimica Acta 26A (1970) 2207-2215.

[9]. V.A.M. Brabers, Physical Status Solidi A 12 (1972) 629-636.