

PHOTOCATALYTIC DEGRADATION OF NITROARENES USING ACTIVATED CARBON / TiO₂ PHOTOCATALYST

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Activated carbon is one of the most important green materials used in several environmental issues. The activity of the activated carbon could be further enhanced through the impregnation of some metal oxides, preferably the photocatalytic semiconductors like oxides of titanium, tungsten, zinc, iron, manganese, which are known as the semiconductor materials. In the present work, the impregnation was carried out under mild hydrothermal conditions ($T < 200^{\circ}\text{C}$) to obtain a highly active carbon/semiconductor composite. Activated carbon was doped with active compounds like TiO₂ and ZnO up to 20 wt %. The effect of crystallization temperature, pH of the media, the type and concentration of the solvent on the resultant product has been studied in detail. The resultant products obtained were characterized through X-ray diffraction, BET surface area analysis, SEM and EDAX studies. The photocatalytic decomposition of nitroarenes like nitrobenzene and *m*-dinitrobenzene has been studied using the impregnated activated carbon/TiO₂ semiconductor composite. Natural sunlight was used as the main light source in the photocatalytic reaction. The possible reaction mechanism for the photocatalytic degradation of nitrobenzene has been proposed here for the first time.

Key words: Activated carbon, photocatalyst support, hydrothermal treatment and impregnation

1. Introduction

Activated carbon has long been recognized as one of the most versatile adsorbent materials used for the effective removal of low concentrated organic and inorganic species from solution and the industrial wastewater. The properties of activated carbon are attributed mainly to its highly porous structure and relatively larger surface area ($>1000\text{m}^2/\text{g}$). Recently some attempts have been made to impregnate semiconductor complexes to porous solid support to prepare the semiconductor/porous solid photocatalyst.^{1,2} According to chemical reaction kinetics, the rate of chemical reactions is determined by the concentration of target substance. Lower the concentration; obviously lower the chemical reaction rate. This means it will take a very long time for organic substances of target to be photodegraded to the desired low levels. The adsorbent makes a high concentration environment of target substances around the loaded photocatalyst by its adsorption, and then the rate of photodegradation will be enhanced.

Impregnated activated carbon having the chemicals finely distributed on their internal surface layers optimizes the existing properties of the activated carbon giving a synergism between the semiconductors and the carbon. This facilitates the cost-effective removal of certain organic impurities, which would be impossible otherwise. For environmental protection, a variety of impregnated activated carbon materials are available and have been used for many years in the fields of gas purification, civil and military gas protection and catalysis.^{3,4,5} There is much scope for the impregnation of a suitable semiconductor onto the activated carbon surface layers to prepare carbon/semiconductor photocatalyst. The adsorption capacities and the feasible removal rates could be

substantially boosted by the impregnation of the activated carbon with suitable semiconductors. When these chemicals are deposited on the internal surface layers of the activated carbon, the removal mechanism also changes. Hence in the present study we have used activated carbon as an inert porous carrier material for distributing TiO₂ and ZnO on the large internal surface, thus making them accessible to reactants for photocatalytic degradation. The photocatalytic degradation of nitrobenzene was carried out successfully using this impregnated activated carbon/TiO₂ photocatalyst. Here the authors have proposed a probable reaction mechanism for the photocatalytic degradation of nitrobenzene for the first time.

2. Experimental

In the present work, commercially available activated carbon (Loba chemie, India) was used along with the coconut shell based activated carbon. Activated carbon was crushed into small particles and separated by 50-80 mesh. First activated carbon was washed with a double distilled water till black color of washings disappeared, followed by soaking in 5% HCl solution with a constant shaking for 24 h. Further it was washed with distilled water till the pH of washings become neutral. Finally the product was dried at about 80°C. Then a required amount of activated carbon (2g) was taken in a teflon liner containing a desired amount (10ml) of different molar concentration of HNO₃ and NaOH as solvents. The active elements such as TiO₂ and ZnO were taken in the form of respective oxides or gels. This mixture was stirred well using a magnetic stirrer for two hours. Later the teflon liner was placed in an autoclave, which was kept inside a furnace provided with a temperature programmer controller. The temperature of the furnace was raised slowly up to a predetermined

temperature (150–200°C) for a period of 8–24h. The experimental conditions for the treatment of activated carbon are given in Table 1. After the experimental runs the autoclaves were quenched using air jet and water and the liners were taken out. The contents of the liners were thoroughly washed in distilled water repeatedly, and centrifuged in order to settle the resultant products, which were later dried in an oven before using it in the catalytic studies.

Table 1. Experimental conditions for the hydrothermal treatment of activated carbon

Sl. No.	Activated carbon: g	Nutrients			Solvent	% Fill	pH	Temp °C	Time h
		TiO ₂ mg	ZnO mg	*TTIP ml					
1	30				1.5 M NaOH	55	8	200	8
2	40				1 M NaOH	55	8	200	12
3	40				1 M HNO ₃	55	4	250	8
4	30				1.5 M HNO ₃	45	3.5	250	12
5	30				1 M HNO ₃	50	4	150	24
6	30				1 M NaOH	45	10	150	24
7				3.7	1 M HNO ₃	55	4	240	6
8				3.7	1 M HNO ₃	55	4	200	12
9		30			1.5 M NaOH	55	8	200	12
10		30			1.5 M HNO ₃	55	4	200	12

*Titaniumtetraisopropoxide

In this way activated carbon impregnated with TiO₂ and ZnO were prepared. Similarly, temperature, concentration of mineralizers and the dopants were also varied in order to facilitate the entry of active complexes onto the activated carbon surface layers, Figure 1 shows the schematic representation of TiO₂ impregnation onto activated carbon.

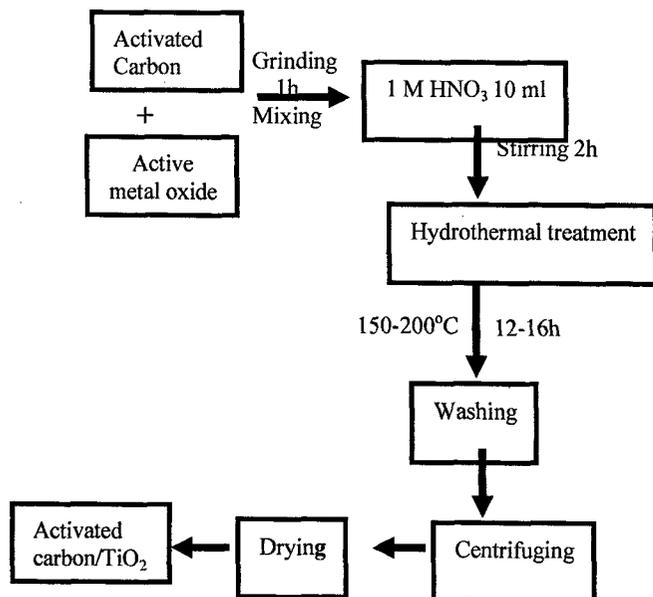


Figure 1. Schematic representation of impregnation of activated carbon.

3. Results and Discussion

3.1 Characterization

It is very important to understand the characteristic properties of activated carbon to explore their applications. Therefore, scientists are deeply concerned to tailor the

properties of activated carbon during the preparation or by impregnation with suitable active complexes to suit a desired application. The characterization describes those features of the composition, surface nature and structure of a material that is significant for the preparation of desired activated carbon for a specific application. Characterization of the activated carbon in this work covers X-ray powder diffraction, determination of the surface area by BET surface area analysis, scanning electron microscopy and EDAX.

3.2 X-ray powder diffraction

X-ray powder diffraction (XRD) has been applied to the characterization of carbonaceous materials including coals for the better understanding of their molecular-level structures and ordered packing of their structural units.^{6,7} The presence of impregnated elements on the activated carbon was detected by this technique. The patterns were indexed and compared with the JCPDS files (PDF No 72-0746 PCPDF WIN version 2.01)⁸ and other literature data. The Figure 2 shows the XRD patterns of untreated activated carbon, impregnated activated carbon/TiO₂ for 8h and impregnated activated carbon/TiO₂ for 24h. As shown in the X-ray patterns the peaks assignable to anatase phase were observed as the main phase. XRD patterns for activated carbon samples indicated gradual changes according to the progress in impregnation. The XRD patterns for activated carbon show peak around $2\theta=25^\circ$, which corresponds to (002) reflection of carbon due to the stacking structure of aromatic layers⁹ (Fig.2a).

From the X-ray powder diffraction studies we have observed the formation of TiO₂ of both rutile and anatase phases during the hydrothermal treatment when TTIP was used as precursor under different pH conditions. Though the rutile phase was dominant in the resultant product, the presence of a small amount of anatase persisted except when the experimental temperature was around 200°C. Interestingly, rutile phase was formed as a prominent phase with better results in the sense, better photocatalytic activity, because of the monodispersed particles with a high degree of crystallinity. However, the formation of a single homogeneous phase depended upon the proper selection of

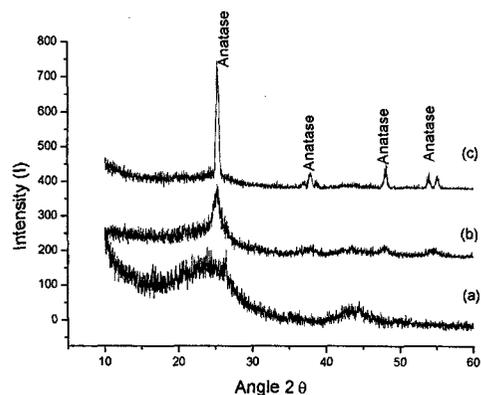


Figure 2. XRD patterns of: (a) untreated activated carbon; (b) impregnated activated carbon/TiO₂ for 8h; (c) impregnated activated carbon/TiO₂ for 24h.

pH of the media and crystallization temperature. We have carried out the impregnation within a wide range of pH of the media (1 to 12). As seen in the Figure 3, rutile phase was dominant when the pH was low (1 to 4), but as pH is increases, the anatase phase becomes prominent with very little amount of rutile. Thus, with the addition of NaOH, the formation of anatase phase was favoured. With the further increase in the pH beyond 12, only an amorphous material was obtained. With an increase in the reaction time there was an increase in the crystallinity of anatase TiO₂.

Similarly we have obtained the activated carbon impregnated with ZnO, and were subjected to X-ray powder diffraction. The representative X-ray diffraction patterns of ZnO impregnated activated carbon are shown in Figure 4.

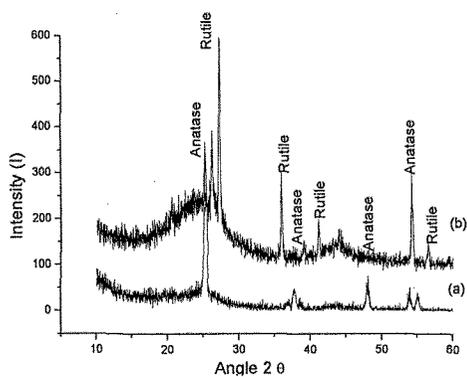


Figure 3. XRD patterns of: (a) anatase phase formation when TTIP was used as precursor for impregnation at pH above 6; (b) rutile and anatase phases at pH 4.5-6.5.

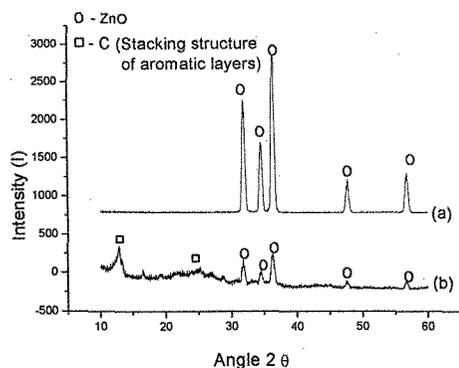


Figure 4. XRD patterns of: (a) pure zinc oxide; (b) activated carbon/ZnO sample after impregnation for 17 h

3.2 BET surface area analysis

The BET surface area measurements were carried out for the impregnated activated carbon using Shimadzu Flowsorb II Model No.2305, Japan. The average specific surface area for the activated carbon impregnated with different active compound is given in Table 2. The specific surface area strongly influences the performance of the impregnated carbon. Higher the impregnation temperature,

larger was the surface area. Since larger surface area offers more active sites for reaction between the active compounds and the organic molecules, more organic molecules could be adsorbed onto these carbon surface layers. The specific surface area decreases as the weight percent of active compound increases as shown in Figure 5. There was a significant change in the surface area when impregnated active elements were less than 30 weight percent, but above 30 weight percent surface area decreased. This may be due to the blocking of pores by these active elements. It was further confirmed by a decrease in the adsorption of the samples that were impregnated with more than 30 weight percent of active complexes.

Table 2. BET surface area of activated carbon

Sl. No.	Sample	BET surface area
1	AC*/TiO ₂	1025.8
2	AC*/ZnO	910.0
3	AC* Untreated	910.8

*AC=activated carbon

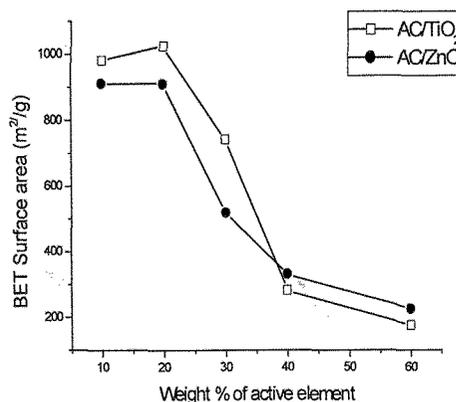


Figure 5. Plot of BET surface area of impregnated samples against weight % of active complexes.

The active complexes are impregnated up to a depth of few atomic layers of the activated carbon surface. The actual process of impregnation of the designer particulates takes place as follows: initially the particles are nucleated on the activated carbon surface. At the same time the solvent will be playing a role of an etchant and due to which the porosity of the carbon is either enhanced or the pore diameter is widened or some carbon atoms are removed creating kinks and voids. These sites on the activated carbon surfaces layers form the ideal sites for the impregnation of the active TiO₂ compound. Such a composite material was later stabilized through a continued hydrothermal reaction. The stability of these designer particulate/activated carbon composites could be verified through repeated cleaning in ultrasonic water bath. A closer and high-resolution SEM studies confirm the impregnation of the TiO₂ and ZnO on the surface atomic layers of carbon. Otherwise, the TiO₂ or ZnO particles would have popped off from the carbon surfaces during repeated ultrasonication.

3.3 SEM and EDAX

The morphology of the resultant products of impregnated activated carbon/semiconductor photocatalyst was studied using SEM and the active complexes that were deposited on the surface was identified by EDAX analysis. Figures 6 & 7 shows the SEM of activated carbon/TiO₂ activated carbon/ZnO prepared by hydrothermal treatment at 200°C for 12h and the EDAX of the titanium oxides deposited on the activated carbon surface as small clusters. The titanium dioxide molecules migrate into the activated carbon pores and crystallize as small clusters, which act as active sites for the reaction with organic molecules within the numerous micropores of activated carbon. The EDAX patterns of the representative parts of the impregnated activated carbon sample are shown in the Figure 6. The TiO₂ crystals entered up to several micron depths of the activated carbon surface layers and were non-uniformly distributed on the activated carbon pores and surface layers. The enlarged portion of the Figure 6a is shown in the Figure 6b, which shows the TiO₂ crystals that are deposited in the macropores of the activated carbon. The crystallinity of TiO₂ increased with an increase in the crystallization temperature. The temperature, 180-250°C was found to be suitable for the better crystallization of TiO₂ as well as other active compounds like ZnO.

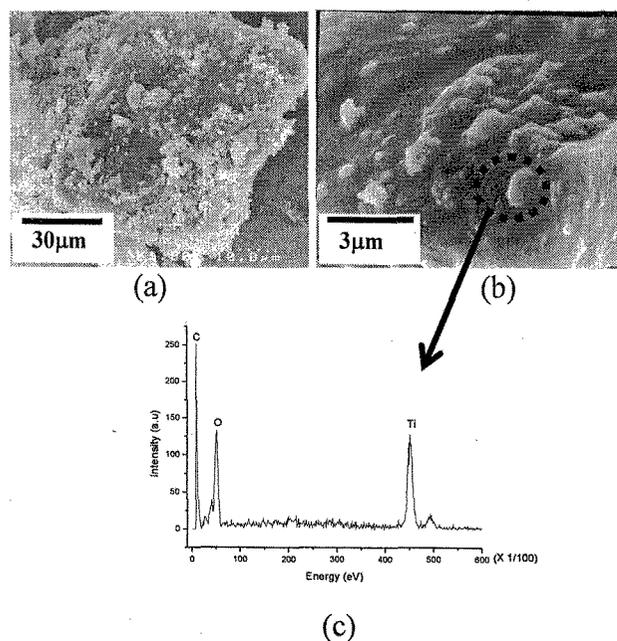


Figure 6. SEM photograph of activated carbon/TiO₂ sample with EDAX spectra: (a) deposition of TiO₂ crystals on the activated carbon; (b) a part of the activated carbon enlarged, showing TiO₂ deposition; (c) EDAX spectrum of the enlarged part.

4. Photocatalytic degradation of organic pollutants

The onsite treatment of effluent contaminated with toxic organic compounds frequently involves their vaporization, which needs to be controlled to avoid emissions of these contaminants to the atmosphere. The volatile organic compounds (VOCs) thus removed could be controlled through different methods. The most common ones are

incineration, biofiltration, carbon adsorption and catalytic oxidation.¹⁰ Recently Mataos et al. (1998)¹¹ degraded phenol as an aromatic molecule at room temperature using suspended mixture of TiO₂ and activated carbon via photocatalytic oxidation. Though they have used photocatalyst, the mechanisms for the photocatalytic degradation have not been studied. Several scientists are working especially on TiO₂ as a photocatalyst for degrading some of the organic compounds present either in the effluent from various industries as well as in soil pollutants. This prompted us to take up this work in detail for the photodegradation of nitroarenes and other organic molecules using activated carbon in the presence of photocatalytic TiO₂ and ZnO impregnated onto the activated carbon and propose a probable reaction mechanism for the photocatalytic degradation of nitrobenzene.

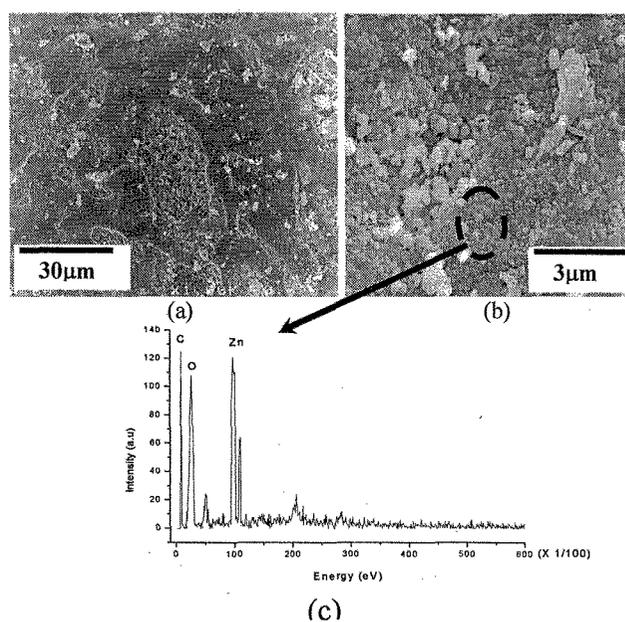
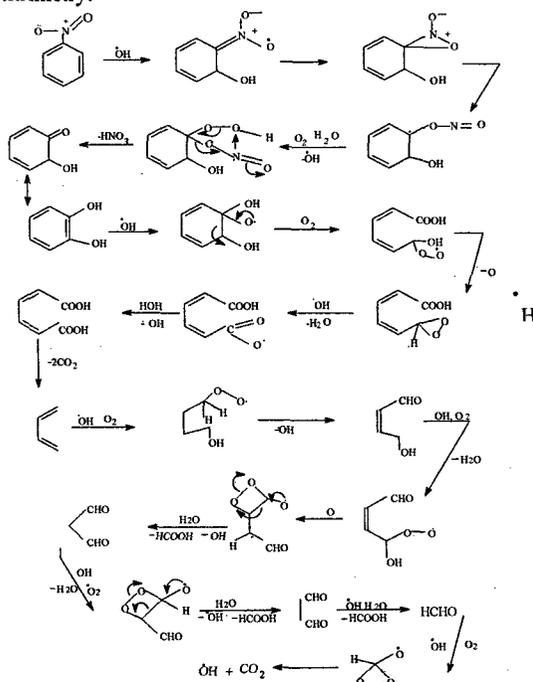


Figure 7. SEM photograph of activated carbon/ZnO sample with EDAX spectra: (a) pores of activated carbon surface with ZnO particles deposition; (b) an enlarged part of the activated carbon pore on which ZnO crystals were deposited; (c) EDAX spectrum of the representative part of the Fig. 7(b)

In the present work nitroarenes like nitrobenzene and *m*-dinitrobenzene were chosen for degradation, using activated carbon as photocatalyst support. In many of the photocatalysed conversions, hydroxyl groups are added to the substrate presumably as hydroxyl radical produced at the activated carbon surface. It has been established in gas-solid studies that alcohol binds to activated carbon surface more strongly than the aromatic hydrocarbon. By extension, the polyhydroxyl compound generated as intermediates in aromatic conversion, apparently binds very strongly leading to relatively rapid completion of the reaction.

In photocatalytic degradation, solution of nitroarenes (30 ml) in excess alcohol (15 ml) taken in a round-bottomed flask was mixed with a known amount of 0.1N Na₂CO₃ and then diluted with distilled water until turbidity

persists. At this junction, one or two drops of alcohol was added to get a clear solution. To this test solution ~40 mg of different samples of impregnated activated carbon was added and kept under sunlight. Under similar condition, pure activated carbon (without any impregnation) and a blank solution (without activated carbon) were also prepared and progress of the reactions was monitored by TLC at a regular interval. The aliquots of the reaction mixture was removed from both the flasks and extracted into ether separately. Later it was spotted on a TLC plate and developed in different solvent systems. Keeping the TLC plates in an iodine chamber aided identification of spots. After 10-15 hours, decomposition of *m*-dinitrobenzene and *m*-nitrobenzene was observed in case of activated carbon impregnated with TiO₂ and ZnO as catalysts, whereas in the case of pure activated carbon it showed only a partial decomposition. The probable mechanism for the degradation of nitroarenes is given in Scheme 1. It may involve adsorption and photocatalytic decomposition. First adsorption at the active surface followed by the formation of the activated complex CO and then further degradation to liberate HNO₃, H₂O, CO₂, etc. The formation of minerals acids was confirmed by titrimetry.



Scheme 1. Reaction mechanism nitroarenes degradation

In order to confirm the above observation, we have carried out the photocatalytic degradation of the above *m*-nitrobenzene and nitrobenzene using the known photocatalytic TiO₂ and observed identical results. The catalyst impregnated with TiO₂ and ZnO were more effective than the untreated activated carbon for the

nitroarenes decomposition. This confirms the efficiency of the prepared catalysts.

Conclusion

Impregnation of activated carbon as photocatalyst support was carried out under mild hydrothermal conditions (T-150-200°C). The type of active compound plays a very important role in the photocatalytic properties of impregnated activated carbon. The active compounds such as TiO₂ and ZnO have showed good photocatalytic activities. An increase in the temperature resulted in the good crystallinity of active compounds that were deposited on the activated surface, and these samples showed higher photocatalytic performance than the samples impregnated at lower temperatures.

The experimental duration of impregnation also plays a very important role in improving the impregnation and obtaining higher photocatalytic activity. Increase in the impregnation time increases the crystallinity of active compounds that are deposited onto the surface layers of carbon, which resulted in the good photocatalytic activity.

The formation of a single TiO₂ phase depends upon the proper selection of pH of the media and crystallization temperature when TTIP was used as the starting material. The rutile phase was dominant when the pH was low, 1-4, but with an increase in the pH, anatase phase becomes prominent forming a very little amount of rutile. Thus with the addition of NaOH, the formation of anatase phase was favoured. No phase change has occurred during the hydrothermal impregnation, when commercial TiO₂ was taken as the starting material.

Reference

- [1] H. Yoneyama, T. Torimoto, *Catalysis Today*, 58, p133 (2000)
- [2] Z. Ding, X. Hu, P.L. Yue, G.Q. Lu and P.F. Greenfield, *Catalysis Today*, 68, p173 (2001)
- [3] B.J. Park, S.J. Park, and S.K.R. Yu, *Proceedings of International Symposium of Carbon Tokyo* (1998).
- [4] A. Gavrilidis, A. Varma and M. Morbidelli, *Catal. Rev. Sci. Eng.* 631-637 (1999).
- [5] I. Prasetyo and D.D. Do, *Carbon* 37 12 p 1909-1918 (1999)
- [6] L. Cartz, R. Diamond and P.B. Hirsch, *Nature* 177 p.500 (1956).
- [7] D.L. Wertz, *Energy Fuels* 13 p 513. (1999).
- [8] Powder Diffraction File, Card No. 84-1285, 84-1284, 80-0075, 80-0074 and 83-0951, 1998 JCPDS-International Center for Diffraction Data. PCPDFWIN V. 2.01.
- [9] N. Yoshizawa, K. Maruyama, Y. Yamada and M.Z. Blajet, *Fuel* 79 (12), p1461 (2000)
- [10] M.C.M Alvim Ferraz, S. Moser, and M. Tonhaeuser, *Fuel* 78 p1567 (1999)
- [11] J. Mataos, J. Laine and J.M.Herrmann, *Applied Catalysis B: Environmental* 18, p281 (1998).