Research Article

Study of Methylene Blue Degradation by Gold Nanoparticles Synthesized within Natural Zeolites

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We carried out the *in situ* synthesis of gold nanoparticles inside a natural clinoptilolite-type zeolite matrix, using ascorbic acid as reducing agent. The microstructure of both zeolite and zeolite-gold nanocomposite was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Scanning Transmission Electron Microscopy (STEM), and Energy-Dispersive X-ray Spectroscopy (EDS) techniques. Size distribution as assessed by STEM indicated that 60% of gold nanoparticles measured less than 2.5 nm. Determination of the surface area by the BET method revealed a specific value of 27.35 m²/g. The catalytic activity of zeolite-gold regarding methylene blue degradation under different light-exposing conditions was evaluated by UV-Vis spectroscopy. The results indicated that 50% degradation was achieved in only 11 min in presence of sunlight. This reaction was faster in comparison with those obtained using a white LED light. A notable aspect of this study is that catalysis was carried out without the addition of any strong reducing agents, such as sodium borohydride (NaBH₄).

1. Introduction

Currently, the serious air, ground, and water pollution problems pose enormous challenges in the area of catalysis [1]. In this regard, the catalytic processes occurring naturally in our environment should serve as an example for designing and developing new catalysts. The development of these new catalysts pursues to improve their activity and selectivity while decreasing by-product generation, as well as that of other pollutants. Catalysis classification is based on the interaction between the phases comprising the system. Heterogeneous catalysis takes place when a solid phase (macroscopic catalyst) interacts with a liquid phase system. Regarding homogenous catalysis, the interaction occurs between two liquid phases (at the macroscopic level). Currently, the most used catalysts in industry are those of the heterogeneous type [2]; they stand out for several reasons such as selectivity, their long lifespan, and their ability to be

reused. Because of these reasons, the most suitable supporting materials for heterogeneous catalyst manufacture are those possessing high porosity and consequently a high surface area.

Catalytically active material is laid on surfaces such as natural and synthesized aluminosilicate, metal oxides, and activated carbon. All of these are commonly used for this purpose [3, 4]. These materials function as support for nanocatalysts and exert a heterogeneous catalytic effect, thereby creating a synergy by inducing an interaction [5] between the components (zeolites and nanoparticles, in this case). This renders the catalytic processes even more efficient. In addition, nanomaterial confinement produces different effects on the catalytic response displayed by the materials laid on the supporting surface [6–8].

On the other hand, several industries such as those processing textiles, paper, and leather use dyes in order to add color to their respective products. They also consume

considerable amounts of water and consequently they induce massive pollution [9]. Particularly, the cationic compound methylene blue (MB) is the most used dye in order to process different types of textiles such silk, cotton, and wool [10–12]. This dye represents a health hazard for both humans and animals. Therefore, it must be removed from the water that has been already polluted by industrial activity [13, 14]. Among the alternatives for dye-polluted water remediation, adsorption methods have additional advantages regarding other processes as their cost is low, they are easy to operate, and they do not release toxic substances into the process [15].

In this work, a natural zeolite (clinoptilolite type) was used as supporting material [16–18]. It has a complex molecular formula: $(\text{Na}, \text{K}, \text{Ca}) 2\text{-}3\text{Al}_3 (\text{Al}, \text{Si}) 2\text{Si}_3\text{O}_{36} \cdot 12\text{H}_2\text{O}$, and it possesses a nanopore array and a high thermal stability, being thus ideal for this purpose. Zeolites are materials possessing pores ranging between 0.5 and 2 nm [19]. Nanometric-sized metallic gold was used as active material whereas ascorbic acid was the reducing agent in order to trigger gold (Au) nanoparticles synthesis [20–22].

A study on the catalytic effect of the obtained zeolite-Au nanocomposite (ncomp zeo-Au) was carried out using MB photodegradation as experimental model [15, 23, 24]. Since illumination plays a major role in catalytic processes [25–27], the experiments were conducted using two different light sources: (a) a LED lamp as source of white light and (b) sunlight. In order to ascertain the contribution of the zeolite matrix devoid of gold nanoparticles on MB catalytic degradation, two experiments using natural zeolite (clinoptilolite) were carried out under the same illumination conditions as described above. Moreover, several authors use the reducing agent NaBH_4 as complement in order to accelerate the catalytic process by directly adding it into the solution to be bleached [28, 29]. However, the use of this compound increases the cost of the catalytic process and it contributes to additional water pollution. Considering all of the above, in this paper we show that gold nanomaterials synthesized within the zeolite matrix have an efficient catalytic activity on MB photodegradation, without needing the addition of yet another compound in order to accelerate catalysis.

2. Materials and Methods

2.1. Materials. All reagents were of AR grade. HAuCl_4 and ascorbic acid were purchased from Sigma Aldrich (99% pure). 18.2 M Ω Milli-Q water was used throughout the experiment. Natural zeolite was a gift from the San Francisco (SF) mine in San Luis Potosi (Mexico).

2.2. Catalyst Preparation. Deposition was the chosen method to prepare the catalyst. In this procedure, the metal salt (aqueous HAuCl_4) was incorporated by adsorption into the supporting material suspension and this occurred because of the interaction between the ions from the metallic compound and the active sites on the supporting material. Solvent excess may be removed by filtration or decantation. The interaction between the active component and the carrier is due to ion exchange between the supporting material

FIGURE 1: Scheme of the deposition method for catalyst preparation: Au nanoparticles supported in zeolites.

and the cationic species (Au^{3+}) in the solution. This catalyst preparation method has the advantage of producing low catalyst charges and also, through the interaction produced by adsorption, it stabilizes the metallic component preventing further catalyst synthesis. Thus, small catalyst particles appropriately dispersed on the surface of the supporting material were obtained. All of this renders this method suitable to perform the deposition of noble metals. The elevated cost of the catalyst is concomitantly reduced as small percentages are used while achieving a considerable dispersion on the supporting material's surface. Figure 1 shows the synthesis scheme.

Ten grams of zeolite, previously ground in an agate mortar, was placed in a 100 mL glass flask. Initially, a 40 mL volume of the metallic precursor (0.01 M HAuCl_4) was added and the mixture was homogenized by vortexing for 5 min at 2400 rpm. The sample was stored for 1 h to allow the impregnation of the zeolite and the supernatant (still turbid) is removed after this period. Afterwards, 10 mL of reducing agent (ascorbic acid 0.1 M) was added in order to induce precipitation. The obtained dispersion was vortexed at 2400 rpm for 5 min to ensure homogenization. The sample was covered with aluminum foil to avoid ascorbic acid photooxidation. The recovered solid was placed in a glass Petri dish and subsequently dried in an oven at 55°C for 24 hours. The material removed from the oven was crushed again in an agate mortar to perform the nanostructural study and to evaluate its catalytic activity. The net gold percentage in the zeo-Au composite was 0.7% (normalized weight).

3. Results and Discussion

3.1. X-Ray Diffraction. Both the ncomp zeo-Au system and the zeolite matrix were characterized by X-ray diffraction

FIGURE 2: Comparison of X-ray diffraction patterns for natural zeolites and ncomp zeo-Au.

using PANalytical Empyrean Series 2 equipment possessing a Pixel^{3D} high-resolution detector. The experiments were run from 10 to 80 degrees with a 0.013° step, a 60 kV operating voltage, and $\text{CuK}\alpha$ ($\lambda = 1.54060 \text{ \AA}$).

In Figure 2 the X-ray diffraction patterns of pure zeolite and zeo-Au are observed. The software X-Pert High Score (PANalytical) was used for analysis and identification of the crystalline phases. The results indicate that the obtained diffractogram for the pure zeolite sample corresponds to the crystalline structure of clinoptilolite, having the molecular formula $\text{H}_{42.64}\text{Al}_6\text{Ca}_{1.24}\text{K}_{1.76}\text{Mg}_{0.2}\text{Na}_{1.84}\text{O}_{93.32}\text{Si}_{30}$ and identified with the data card number 98-010-0096 in the Inorganic Crystal Structure Database (ICSD). Besides clinoptilolite, in the diffractogram obtained for the zeo-Au sample, two peaks at 38.15° and 44.37° were identified corresponding to the (111) and (200) family of planes of gold fcc structure, respectively (ICSD 98-004-4362).

3.2. Scanning Electron Microscopy (SEM). SEM was performed using a Hitachi microscope (5500 model). Samples were prepared by dispersion in water using an ultrasonic bath. Subsequently, a drop of the dispersed solution was laid on a copper grid and stored at room temperature to allow drying. The obtained SEM micrographs (Figure 3) showed Au supported in zeolite. The crystal morphology of zeolite is observed as well as the presence of particles of approximately 5–7 nm size homogeneously distributed on the surface. This observation suggests that these quasispherical-shaped particles are smaller regarding zeolite crystals. This will be confirmed by further tests.

After performing an EDS analysis, Figure 4(a) shows that, besides zeolite components such as aluminum (Al), silicon (Si), and oxygen (O), the Au signal is also present. The Cu signal corresponds to the copper grid used to place the sample. Signals derive from most of the swept surface (Figure 4(b)), showing that gold is evenly distributed on most of the zeolite's surface as shown in the mapping image (Figure 4(c)).

3.3. Scanning Transmission Electron Microscopy (STEM). To perform the STEM analysis, a JEM-ARM200F (JEOL, USA) microscope equipped with aberration corrector CEOS Cs operated at 80 kV was used. To conduct this study, samples of ncomp zeo-Au were prepared by sectioning using an ultramicrotome. The sample powder, previously ground in an agate mortar, was embedded in 1 mL of epoxy resin (Epon-LX112/DDSA/NADIC Methyl/DMP-30) polymerized for 24 h at 60°C and it was subsequently sectioned using an ultramicrotome (Leica Reichert Ultracut S), with a Diatome Ultra 45° knife. The obtained sections were 90 nm thick.

Figure 5 shows dark field (a–d) and bright field (e–h) STEM micrographs. These show the presence of quasispherical nanoparticles between 1 and 5 nm of diameter. In this study, particles under 5 nm are observed. However, this observation was not possible through the SEM study as its resolution is low. The presence of gold nanoparticles on the zeolite sections indicates the presence of gold within its structure. A higher magnification of the ncomp zeo-Au sample is shown in Figure 6. In the latter, gold nanoparticles appear in the zeolite structure. Size distribution of gold nanoparticles indicates that 60% of them measure less than 2.5 nm.

3.4. Specific Surface Area. Specific surface area by the Brunauer-Emmett-Telle (BET) method was determined with Gemini VII 2390 (Micrometrics). The nitrogen adsorption-desorption isotherms were acquired at -196°C . The natural zeolite showed a surface area of $21.90 \text{ m}^2/\text{g}$, whereas the ncomp zeo-Au presented a specific value of $27.35 \text{ m}^2/\text{g}$. This increment in the specific surface area in comparison with control sample was attributed to the functionalization of zeolite with Au nanoparticles. It is important to notice that the zeolites were not treated with any harsh acids nor high temperatures that in cases may increase the surface area of materials.

3.5. Photocatalysis. Photocatalysis is generated from the interaction between light and semiconductive or conductive nanoparticles [23, 30]. The wavelengths associated with the photocatalytic activity of semiconductor nanoparticles are mainly those in the near UV region (as the case of TiO_2), whereas the visible region is associated with the optical absorption of metal nanoparticles (e.g., gold and silver) and thus with their photocatalytic activity. In this work the catalytic activity of natural zeolite and ncomp zeo-Au was evaluated using MB as experimental model. The study was performed using UV-Vis spectroscopy (Perkin-Elmer Lambda 45) in the range between 900 nm and 200 nm in order to monitor optical absorption changes of a MB aqueous solution (0.33 mM) through time. The studies were conducted under two different light-exposure conditions: (a) using a LED white light lamp (high brightness) (2000 lumens and 25 W) and (b) under the sunlight. To study the catalytic activity, the samples were ground in an agate mortar in order to obtain a fine powder such as talc and they were placed in small bags made out of filter papers ($1.5 \text{ cm} \times 1.5 \text{ cm}$), which were subsequently sealed. The bags containing 0.15 g of sample were introduced in transparent glass containers with

FIGURE 3: SEM micrograph of Au supported in zeolite (a) and zoom of a region (b).

FIGURE 4: EDS analysis of Au supported on zeolite: (a) all zeolite components, (b) scan of a surface area, and (c) even distribution of Au.

the MB solutions (30 mL), thus ensuring the contact between materials and solution. To initiate catalysis, the flasks were placed at a 10 cm distance from the LED light. Periodically, a volume of the MB solution was withdrawn in order to obtain its UV-Vis absorption spectrum. To quantify catalytic activity, the absorption decrease was monitored through time at 664 nm. This wavelength corresponds to the strongest absorption for MB. This same procedure was followed in order to evaluate the catalytic activity mediated by sunlight. Solar irradiance for conducting experiments in Hermosillo, Sonora (Mexico), was 6 KWh/m². As shown below, the results indicate that catalysis is more efficient regarding ncomp zeo-Au in the presence of sunlight. The characterization of these synthesized materials shows that nanomaterials are well below 2 nm and thus they may be located within its pores, which are a particular feature of these zeolites, thus enhancing catalytic efficiency.

The MB degradation percentage was calculated according to (1), where A_0 is absorbance at $t = 0$ and A is absorbance at time t . They were both measured at 664 nm:

$$\%D = \left(\frac{A_0 - A_t}{A_0} \right) \times 100. \quad (1)$$

To calculate MB photobleaching ratio, the Langmuir-Hinshelwood equation was used, which is expressed in (2) [31] as follows:

$$\ln \frac{A}{A_0} = -kt, \quad (2)$$

where k is the first-order rate constant of the photodegradation reaction, calculated as the slope of the regression plot $\ln(A/A_0)$ versus irradiation time t ($\ln(A/A_0)$ versus t). All the absorbance values represented in the graph were obtained at 664 nm.

3.6. Increased Rate of Catalysis (Sunlight). Photocatalysis under the sunlight is a technique that allows using a natural resource to increase the catalytic rate [2, 27, 32]. Sunlight is comprised of approximately 43% visible light, whereas only 5% of it is ultraviolet light and the rest belong to the range of infrared light [2]. The UV-Vis spectra shown in Figure 7 correspond to MB degradation as a function of time and under different light-exposure conditions in the presence of two different catalytic agents. In Figures 7(a) and 7(c) MB degradation is observed in contact with the zeolite matrix (without nanoparticles) when illuminated with white light LED and sunlight, respectively. Similarly, Figures 7(b) and 7(d) show MB degradation through heterogeneous catalysis with ncomp zeo-Au in the presence of white light (LED) and solar light, respectively.

Based on the maximum absorption of each spectrum at 664 nm in Figure 7, we obtained curves of MB degradation activity for each case. Figure 8 shows that degradation is faster under the sunlight (Figures 8(c) and 8(d)) in comparison with LED illumination (Figures 8(a) and 8(b)). Similarly, it shows that gold nanoparticles presence in zeolites accelerates MB degradation (Figures 8(b) and 8(d)) compared with the pure zeolite (Figures 8(a) and 8(c)). Through comparison, the required time to achieve 50% of MB degradation is related for each curve. Figure 8(d) shows that the curve representing the more rapid MB degradation corresponds to the ncomp zeo-Au catalyst illuminated with sunlight, reaching a half degradation time of $t_{D50} = 11$ min. Conversely, the slowest

FIGURE 5: STEM micrographs of Au supported on zeolite: dark field (a–d) and bright field (e–h).

FIGURE 6: Higher magnification of STEM micrographs (a and b) and size distribution of Au nanoparticles supported in zeolite.

degradation rate corresponded to zeolite without nanoparticles (Figure 8(a)), where $t_{D50} = 100$ min.

In Figure 9, $\ln(A/A_0)$ versus t plots were constructed, in which k values as derived from (2) are observed. The graphs display the same relationship as in Figures 7 and 8. As shown in Figure 9, the data show a good linear correlation and the slopes calculated from the linear regression fit provided us with the value of the photodegradation reaction constants for each case. In Table 1 the most important data characterizing the reactions of MB photodegradation are summarized. It shows that the highest efficiency is obtained for MB degradation with ncomp zeo-Au matrix

and photocatalyzed with sunlight. Gold nanoparticles present characteristic optical properties, particularly surface plasmon resonance (SPR) in the UV-Vis region. SPR effects arise from coupled oscillation of conductive electrons on the surface of nanoparticles caused by incident electromagnetic radiation. Recently, the presence of an absorption peak in the UV region associated with the interband excitation of electrons from level $5d$ to $6sp$ was demonstrated, and its intensity showed a close correlation with SPR, specially for nanoparticles with diameters below 2.5 nm [33]. Zhu et al. observed in Au nanoparticles supported on zeolites that the UV absorption peak produces a higher superficial photocurrent than the SPR

FIGURE 7: UV-Vis spectra of MB degradation. Natural zeolite: illuminated with LED (a) and sunlight (c); ncomp zeo-Au: illuminated with LED (b) and sunlight (d).

absorption in the Vis region [34]. The model proposed in this paper indicates that zeolites absorb oxygen in their pores and excited electrons on the surface of Au nanoparticles, causing formation of O_2^- species. As consequence of the electron transfer, a partially positive charge is generated in the $5d$ level promoting electron transfer. Then, the Au nanoparticles take the equivalent electrons from absorbed organic molecules to neutralize their positive charge. The mechanism proposed supports our observations of a higher degradation rate of methylene blue with sunlight in comparison with white light. As control, the same catalytic reaction was performed protected from light. After 24 h, the control showed less than 10% degradation of methylene blue, confirming that the catalytic reaction is dependent on light.

Furthermore, the z potential was also measured for both pure zeolite and ncomp zeo-Au systems and the respective values are shown in Table 2. In both cases, the system had a substantial negative electrostatic charge interacting

with the positive charge of MB and causing electrostatic interactions between dye and the catalyst molecules. This may be a determinative factor for the efficient catalysis mechanism. It should be noted that the results obtained for the catalytic activity do not include the addition of compounds enhancing the degradation reaction, such as sodium borohydride. However, it was assumed that residual ascorbic acid molecules derived from the *in situ* synthesis of gold nanoparticles remain in the ncomp zeo-Au. Thus, the addition of another reducing agent is not necessary when catalyzing MB degradation.

4. Conclusions

The processes and methods implemented in these systems intended to clean water include green materials only: ascorbic acid and natural zeolites. The production of a nanomaterial as small as possible, encompassing a larger surface area, is

FIGURE 8: Percentage of MB degradation and the time period to achieve 50% degradation. Natural zeolite: illuminated with LED (a) and sunlight (c); ncomp zeo-Au: illuminated with LED (b) and sunlight (d).

TABLE 1: Parameters for each system: percentage of total degradation ($\%D_t$), degradation ratio (k), and time to achieve 50% degradation (t_{D50}).

Sample (0.15 g)	$\%D_{t \rightarrow \infty}$	$k \text{ (min}^{-1}\text{)}$	$t_{D50} \text{ (min)}$
Zeo (LED light)	70	0.008	100
Zeo-Au (LED light)	87	0.04	15
Zeo (sunlight)	100	0.02	26
Zeo-Au (sunlight)	100	0.07	11

needed in order to obtain an enhanced catalytic activity. In this case, the characteristic matrix pores of the natural zeolite can be employed as cavities in which nanomaterials (particles or clusters) are synthesized and confined. The results obtained by transmission electron microscopy in scanning

TABLE 2: Physicochemical properties: pH, conductivity, and zeta potential of natural zeolite and ncomp zeo-Au.

Sample (0.15 g)	pH	Conductivity ($\mu\text{S/cm}$) $T = 25^\circ\text{C}$	z potential (mV)
Zeo	6.914	28	-37
Zeo-Au	5.973	103.7	-29

mode (STEM) using the synthesized samples sectioned in nanomaterials by ultramicrotome confirm that nanoparticles under 2 nm are housed inside the pores of the zeolites.

This synthesis is considered as sustainable chemistry as it is performed at room temperature (20°C – 25°C) and using ascorbic acid as reducing agent; therefore it does not generate

FIGURE 9: Ratio of MB degradation in samples; natural zeolite: illuminated with LED (a) and sunlight (c); ncomp zeo-Au: illuminated with LED (b) and sunlight (d).

environmental pollution. The degradation of MB by the synthesized nanomaterials is performed at room temperature without using a reducing agent, for example, sodium borohydride (NaBH_4). Therefore, this method reduces the cost of the process and the environmental impact. The catalysis presented in this study is of the heterogeneous type; thus ncomp zeo-Au matrix can be reused in other catalytic cycles by simply removing the container in which the material is confined.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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