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ATMOSPHERIC NANOPARTICLES IN PHOTOCATALYTIC AND THERMAL PRODUCTION OF ATMOSPHERIC POLLUTANTS

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ABSTRACT

Atmospheric aerosols which occur above heavily polluted areas such as Mexico City, are characterized and found to be complex materials that have the potential to accelerate important ozone-forming reactions photocatalytically and thermocatalytically. In addition, because the particles are respirable, they may represent a considerable health hazard. The aerosols consist of two intermixed components. The first component consists of amorphous carbonaceous materials of variable composition with "fullerene like" materials dispersed throughout. The second component is an inorganic material consisting of nanoparticles of oxides and sulfides "supported" on clay minerals. This inorganic component has all of the characteristics of an airborne photocatalyst.

Nanoparticles of Fe₂O₃, MnO₂ and FeS₂ have demonstrated catalytic properties, particularly when they occur in the nanoparticle range, as they do in the subject aerosol materials. These materials have band-gaps that occur in the broad solar spectrum enhancing the photocatalytic adsorption of solar radiation beyond that of the wider band-gap aluminosilicate and titanate materials, which also occur in aerosols. In addition, the materials are acidic and probably are coated with moisture when suspended in air, further enhancing their catalytic ability to crack hydrocarbons and create free radicals.

Keywords: atmospheric nanoparticles, photocatalyst, atmospheric pollutants

INTRODUCTION

Contaminated cities suffer from high levels of airborne particles which, during adverse weather conditions, form visible clouds suspended above the cities as seen over Ciudad Juarez in Figure 1. In addition to the catalytic effects suggested in this report, particles of the type described also are believed to have adverse public health effects. The United States Environmental Protection Agency (USEPA) has recently reported that particulate matter smaller than 10µm (PM-10) increased the level of respiratory illness in children exposed to levels of 40-58 µg/m³ for extended periods (EPA, 1993). USEPA has recently proposed to further restrict particles smaller than 2.5µm (PM-2.5) (*Chemical and Engineering News*, 1997). Additionally, these airborne particulates and the associated polluting molecules are held responsible for a general degradation in the quality of life in these cities, for example, deterioration of monuments and buildings,

visibility degradation, and acid rain. In spite of the negative impact of air particulates little is known regarding their composition and properties, especially for those particles that fall below 2.5 μm . Recently, a call for more structural and chemical information about these particles has appeared (Abelson, 1997). In this report, we characterize nanoparticles present in aerosols from Mexico City and emphasize the possible role of these atmospheric nanoparticles in photocatalytically producing alkyl free radicals and accelerating other reactions discussed below.

We present evidence that particles smaller than 2.5 μm can play an important, but as yet undetermined, role in catalytically accelerating or guiding atmospheric reactions that occur in polluted air. The importance of excess hydrocarbons (HCs) and nitrous oxides (NO_x s) from vehicular emissions in producing ozone has long been recognized (National Research Council, 1991). Recently, Blake and Rowland (1995) have pointed to the role of leaking alkane hydrocarbons from liquefied petroleum gas (LPG) in increasing the amount of ozone produced over Mexico City. The authors present evidence for very high concentrations of C3 and C4 alkanes and reactive olefinic and acetylenic products from incomplete combustion of LPG and conclude that these molecules play a major role in the production of ozone in the Valley of México. It is likely that a similar situation exists in many other cities where LPG use is high.

The role of catalytic surfaces present in atmospheric aerosols has not been well studied and little appears in the literature regarding the role of indirect photocatalytic pathways. The general role that photocatalytic particles play in global atmospheric chemistry has been reviewed by Zamaraev, et al. (1994). The presence of a photocatalyst permits photoreactions to occur within the main spectral range of available sunlight. Atmospheric nanoparticles arising from disturbed soil particles (and other sources) are expected to contain photocatalysts that affect key reactions. The major solid component of atmospheric aerosols are nanoparticulate silicates, which adsorb short wavelength light. The concentration of such particles is highest in dry areas with values in the neighborhood of 100 mg/m³. Surface areas of these atmospheric nanoparticles are reported to be within the range that characterize heterogeneous catalysts (10-100 m²/gm). The particles are located primarily near the earth's surface and are usually covered with an adsorbed layer of water, which is important in considering potential photocatalytic pathways. Additionally, the presence of sulfur in heavily polluted areas leads to the formation of sulfuric acid, which creates an acidic environment in the encapsulating water layer.

Zamaraev further points out that adsorption of a quanta of light above the bandgap causes excitation of an electron from the valence band to the conduction band, with this excited electron acting as a reductant and the hole in the valence band acting as an oxidant. Compounds with bandgaps appearing in the solar spectrum region such as Fe_2O_3 (2.2eV) and TiO_2 (3.0eV) are known photocatalysts and appear in the atmosphere. Frei (1996) has reported that visible light and O_2 are all that are required to partially oxidize hydrocarbons that are trapped in a zeolite. Recently, Vinodgopal et al. (1996) reported the photosensitized destruction of dyes on semiconductor surfaces such as TiO_2 in the presence of oxygen.

MATERIALS AND METHODS

Samples reported in this study were collected using high volume samplers as previously described (Aldape, et al., 1991a; Aldape, et al., 1991b; Aldape, et al., 1993). Six samples were collected at six sites in Mexico City: Nezahualcoyotl (A), Portales (B), Taxqueña (C), Nezahualcoyotl II (D), Hangares (E), and Secretaria de Hacienda (F). The samples were collected during the winter months when pollution in Mexico City is at its highest forming a cloud similar to that seen in Figure 1. The samples were analyzed with XFA (x-ray fluorescence analysis), transmission electron microscopy (TEM), and IR (infrared spectroscopy). The powders from the filters were directly suspended in isopropyl alcohol using an ultrasonic bath. A drop of solution was placed on a 200-mesh copper grid (covered with a thin carbon layer) and air dried. Samples were examined using a JEOL 4000-EX high resolution microscope. Some of the images were computer processed to increase the signal to noise ratio. Electron diffraction patterns were measured using a CCD camera and analyzed using standard commercial software. Samples were also examined with an SEM JEOL 6400 and a JEOL 2010-EX microscope fitted for x-ray fluorescence analysis. Samples were also examined by infrared spectroscopy (IR) in KBr pellets using a Perkin Elmer Model 238B spectrometer.

RESULTS AND DISCUSSION

Both Mexico City, Mexico (>7000ft.), and El Paso, Texas/Juárez, Mexico (>4000ft.), are at high altitudes surrounded by mountains confining air movement resulting in frequent atmospheric inversions, especially in cold seasons. Both cities sustain large populations, concentrated vehicular activity, and concentrated industrial activity. Particulate input to the

environment due to the above activities is high, creating aerosols of nanoparticles. The composition of aerosols (respirable fraction $< 2.5\mu\text{m}$) over Mexico City has been studied in a series of recent articles (Aldape, et al., 1991a; Aldalpe, et al., 1991b; Aldalpe, et al., 1993). Elemental analysis was performed using the Proton Induced X-ray Emission (PIXE) technique and the most abundant elements found were typical of soil components (Si, Al, Ca, K, Ti, Mn, and Fe). Anthropogenic elements were also found (soot, S, Cu, Zn, and Pb). Anthropogenic material (soot) is approximately represented by the carbon analysis and was found to be in the range of $1-11\ \mu\text{g}/\text{m}^3$. Inorganic material (soil) is approximately represented by silicon analysis and was found to be in the range of $0.2-9.0\ \mu\text{g}/\text{m}^3$. The amount of anthropogenic vs. soil components of the aerosol varied widely but was generally in the neighborhood of 50%. Seasonal variations were observed with maximum values occurring in fall and winter. Daily values show a systematic increase in concentrations during the morning period. Levels were compared with levels found in Los Angeles in 1976 prior to the introduction of automotive pollution controls and were generally higher. Total particulate concentrations were in the range of $120\ \mu\text{g}/\text{m}^3$, which compares with global measurements in the range of $65-200\ \mu\text{g}/\text{m}^3$ for wind-driven dust, which is thought to affect global climate. It is also believed that 50% of the global number is a result of human activity (Li, et al., 1996; Tegen, et al., 1996).

A typical SEM image of particles collected over Mexico City is shown in Figure 2 with the corresponding x-ray analysis shown in Figure 3. In the figure, it is possible to see elongated platelet particles and some filaments. X-ray fluorescence analysis was used to identify the chemical composition of the particulate and fibrous materials. Only the fine respirable particles ($< 2.5\mu\text{m}$) were analyzed. It can be seen from Figure 3 how the elements are associated with the various particles imaged by the SEM. Table 1 shows the carbon and silicon analyses for the six samples with four analyses of different portions of the sample. It can be seen from Table 1 that the carbon content lessens as the silicon content increases and we use these measurements as an indication of the amount of soot (carbon analysis) and the amount of soil (silicon) in the sample. Table 2 indicates the full analysis of the samples associated with the highest and lowest values of the carbon analysis.

All other samples follow similar trends and it can be seen from these data that the soil content increases as the soot content decreases. X-ray diffraction was used to identify the main phases present in the dust. In addition, selected area electron diffraction and nanodiffraction in the TEM were used to identify nanoparticles supported in soil or carbonaceous material. Table 3 indicates the crystalline phases in the samples, which were identified by x-ray and electron diffraction. Particle samples from the atmospheric aerosols were also examined by infrared spectroscopy. The resulting spectra were extremely broad indicating very disordered, small particulate material. The major peaks are indicated in Table 4 and are consistent with the data for crystalline phases in Table 3. Composition of the particles is also consistent with reports of composition of these materials in the atmosphere (Vinodgopal, et al., 1996). The pH of an aqueous phase in which particles were suspended was acidic, indicating that acidic oxides were also present as indicated in the IR.

A TEM image of a typical nanocrystalline particle is shown in Figure 4a. The highly defined surfaces can be clearly seen. The size distribution of particles is shown in Figure 4b. Note that the particles have a distribution in the nanometer range with an average particle size around 40nm, as observed in the TEM. Most of the nanoparticles observed in Figure 4a correspond to Fe_2O_3 with some of the particles being other oxides such as MnO_2 and sulfides such as FeS_2 . These nanoparticles are dispersed on clay particles in the micrometer size range much as the active phase of a commercial heterogenous catalyst is dispersed on a support material. Figure 5a shows a high resolution image of nanoparticles in a sample from Hangares. The insert shows some high resolution images of Fe_2O_3 as determined from the lattice spacings. The corresponding size distribution is shown in Figure 5b for particles observed in the HRTEM. Additionally, the material contains large amounts of amorphous carbon. In several areas we found carbon tubes and well-defined onion structures of the fullerene family similar to those reported recently in the literature (Haggin, 1994).

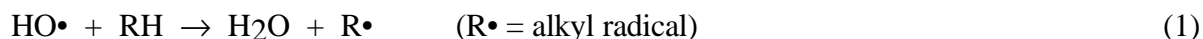
The above data give us a picture of the particulate matter in the Mexico City region as nanoparticulate agglomerates containing high surface area soils (silicates/oxides), semiconducting particles (hematite/pyrite), and other acidic and carbonate solids, probably coated with water. Accompanying these particles is an approximately homogeneous distribution of carbonaceous materials.

Atmospheric aerosols that occur above heavily polluted areas are complex materials that have the potential to accelerate important ozone-forming reactions photocatalytically and possibly thermocatalytically (Zamaraev, et al.,1994). In addition, there is abundant evidence for deleterious health effects from inhaled particles in this size range (*Chemical and Engineering News*, 1997). The particulate aerosols consist of two intermixed components, inorganic and organic as described above. The organic component consists of amorphous carbonaceous materials of variable composition with “fullerene like” materials dispersed throughout. The origin of this component is generally attributed to soot production from burning hydrocarbon-based fuels. The carbon-based component of these aerosols will be the subject of a future article.

The inorganic component consists of nanoparticles of oxides and sulfides supported on clay materials on clay minerals. Additionally, there is a considerable amount of sulfur present, rendering the materials acidic in the presence of water. The origin of this component is generally thought to be from wind-blown dusts created naturally, or by human activity such as vehicular traffic or quarrying operations. This inorganic component has all of the characteristics of an airborne photocatalyst.

Nanoparticles of Fe_2O_3 , MnO_2 , and FeS_2 have demonstrated catalytic properties, particularly when occurring in the nanoparticulate range as they do in the subject aerosol materials. These materials have bandgaps that occur in the broad solar spectrum, enhancing the photocatalytic adsorption of solar radiation beyond that of the wider bandgap aluminosilicate and titanate materials, which also occur in the aerosols. In addition to this, the materials are acidic and are probably coated with moisture when suspended, further enhancing their catalytic ability to crack hydrocarbons and create free radicals.

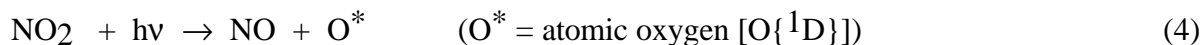
The formation of ozone is not direct but is the result of photochemical interactions of volatile hydrocarbons and oxides of nitrogen (NO_x). Volatile hydrocarbons present in the atmosphere are of many types and follow many different reaction pathways making detailed analysis difficult (Carter, 1994). Blake and Rowland (1995) presented a simplified reaction scheme which starts with the production of alkyl free radicals from hydroxyl free radicals ($\text{HO}\bullet$):



The alkyl radicals then proceed to produce alkyl peroxides which in turn react to produce aldehydes, ketones, and nitrogen dioxide (NO₂).



The NO₂ photocatalytically produces excited atomic oxygen which produces ozone with free oxygen.



The detailed reaction pathway and estimate of rate constants are given in Atkinson (1990). Formation of the radicals in equation 1 is slow due to the high activation energy of hydrogen atom transfer with room temperature rate constants on the order of 10⁻¹⁴ to 10⁻¹⁵ cm³s⁻¹. Under atmospheric conditions, the free radicals are rapidly converted to the peroxyradicals. The peroxyradicals are stable with respect to most atmospheric components and react predominately with NO to form NO₂ (Francisco and Maricq, 1995). Rate constants for alkyl radical formation increase as the carbon chain gets longer, supporting the contention that presence of C₃ and C₄ hydrocarbons accelerate the overall rates. The overall reactivity is thought to be further accelerated by the olefinic and acetylenic content of the atmospheric HCs which appear as additional reactants. The alkyl radical formation should also be enhanced by the presence of catalytic surface.

Atomic oxygen (O{¹D}) is produced photochemically from NO₂ and this reaction has a ΔH^o(298K) of 300 k·J·mol⁻¹ and a λ threshold of 398 nm. Hydroxyl radicals are also formed photochemically with a ΔH^o(298K) of 491 k·J·mol⁻¹ and a λ threshold of 243 nm.



TiO₂ is a well-recognized photocatalyst which completely oxidizes hydrocarbons, photocatalytically producing only CO₂ and H₂O (Hoffmann, et al., 1995). However, the phase and structure are crucial for this to occur effectively. If the TiO₂ is in the rutile phase or other titanium-containing oxide phases are used to photocatalyze the destruction of hydrocarbons, a

considerable amount of “coke” (carbonaceous polymerized fragments) is produced, reducing activity. Thus, ineffective catalysts produce coke and this means the production of carbon-containing free radicals and unsaturated products. The photocatalysts described in this report are relatively poor photocatalysts and are coated with carbon indicating the production of free radicals and partially oxidized products (Cheng, et al., 1995).

Hydroxyl radicals (reaction 6) and peroxide radicals can also be provided by photocatalytic dissociation of water.



Semiconducting oxides and sulfides are known to possess water-splitting activity in aqueous solution (Fox and Dulay, 1993). Gas phase photoreactions of these materials are virtually unstudied. However, the nanoparticles are probably covered with a thin layer of water the reactions may be similar. Nevertheless, these reactions need to be studied experimentally to confirm their importance in the overall scheme.

CONCLUSION

The catalytic role that the materials identified in this report may play in tropospheric chemistry remains to be elucidated and is the subject of a continuing study. But, there is no doubt that the chemistry and physics of these nanoparticulate materials, which occur in increasing amounts over polluted cities, must be understood in greater detail to determine the role they play both in accelerating atmospheric reactions and in creating human health hazards. It is also necessary to understand the role that human vs natural activities play in creating these materials. In this respect, it is worth mentioning the very uniform distribution of nanoparticulate materials. In future studies we will investigate the mechanism by which such uniformity is created.

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Table 1. Atomic weight % carbon and silicon

sample	at. wt. %	1	2	3	4
A	carbon	82.71	85.84	85.03	42.79
	silicon	3.37	2.22	2.82	15.53
B	carbon	57.94	63.38	56.20	72.17
	silicon	11.17	11.52	11.29	4.60
C	carbon	56.35	55.11	61.06	66.39
	silicon	11.28	19.61	7.68	7.39
D	carbon	64.88	65.28	53.32	63.96
	silicon	9.63	11.88	10.64	7.20
E	carbon	59.25	54.31	-	-
	silicon	9.77	10.50	-	-
F	carbon	67.99	77.77	79.12	78.45
	silicon	7.08	4.77	2.46	4.30

Table 2. Atomic weight % of detectable elements

C	O		Na	Mg	Al	Si		P	S	Cl
82.71	9.40		0.70	0.12	0.84	3.37		0.07	0.38	0.04
42.79	28.16		2.15	0.45	4.99	15.53		0.21	0.24	0.05

K	Ca	Ti	Cr	Mn	Fe	Cu	Zn
0.15	0.61	0.07	0.00	0.00	1.11	0.27	0.17
0.78	2.43	0.28	0.00	0.00	1.21	0.42	0.32

Table 3. Chrystalline Phases in Aerosol Samples

Phase	Mineral
$\text{NaAlSi}_3\text{O}_8$	Albite
CaCO_3	Calcite
NaCl	Halite
$\text{Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O}$	Mirabilite
$\text{Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O}$	Natron
$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$	--
NaHCO_3	--
$\text{CaSO}_4 \cdot 2 \text{ H}_2\text{O}$	Gypsum
Fe_2O_3	Hematite
FeS_2	Pyrite
MnO_2	--

Table 4. Infrared Spectrum of Particles from Aerosols

Peak (cm^{-1})	Strength	Attribution (Nyquist, 1971)
3600-2400	broad, strong	water, hydration
2000-1400	very broad, medium	carbonate, water
1250-650	broad, strong	sulfate, silicate, carbonate
600-250	broad, very strong	hematite, pyrite



Figure 1. Dust cloud above Ciudad Juarez, Mexico/El Paso, Texas. Photograph was taken during March 1996 from west El Paso looking south into Ciudad Juarez (courtesy of Dr. L. Murr, Chairman and Professor of Materials Science, University of Texas at El Paso)

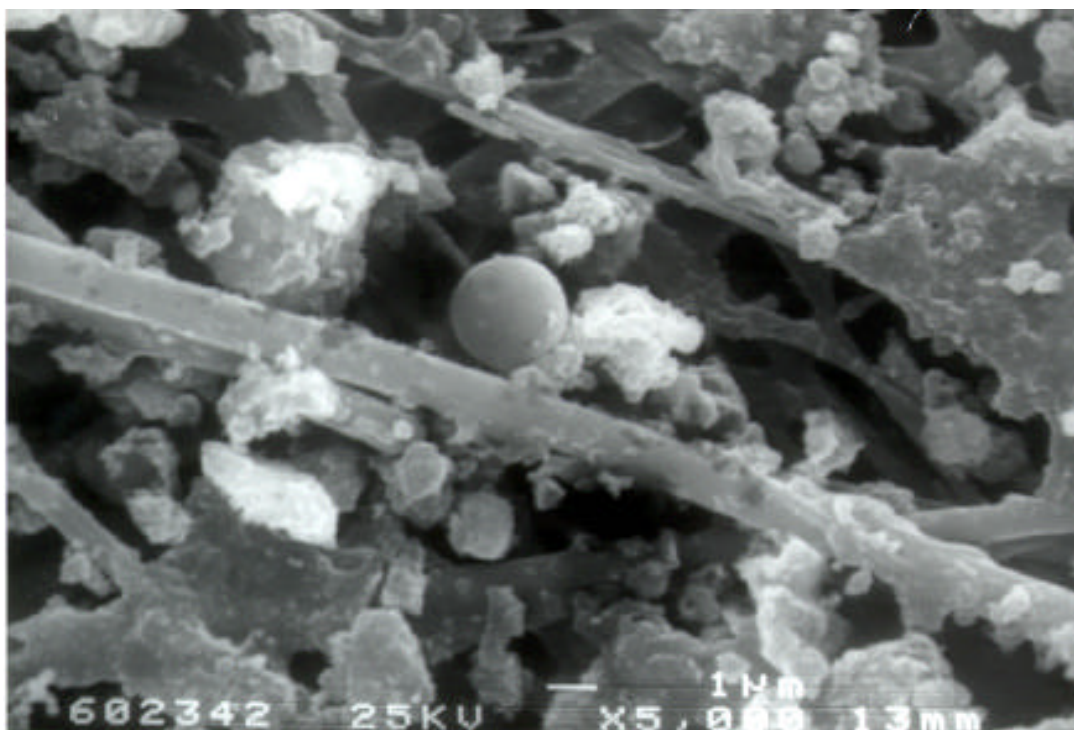


Figure 2. SEM image of typical dust particle.

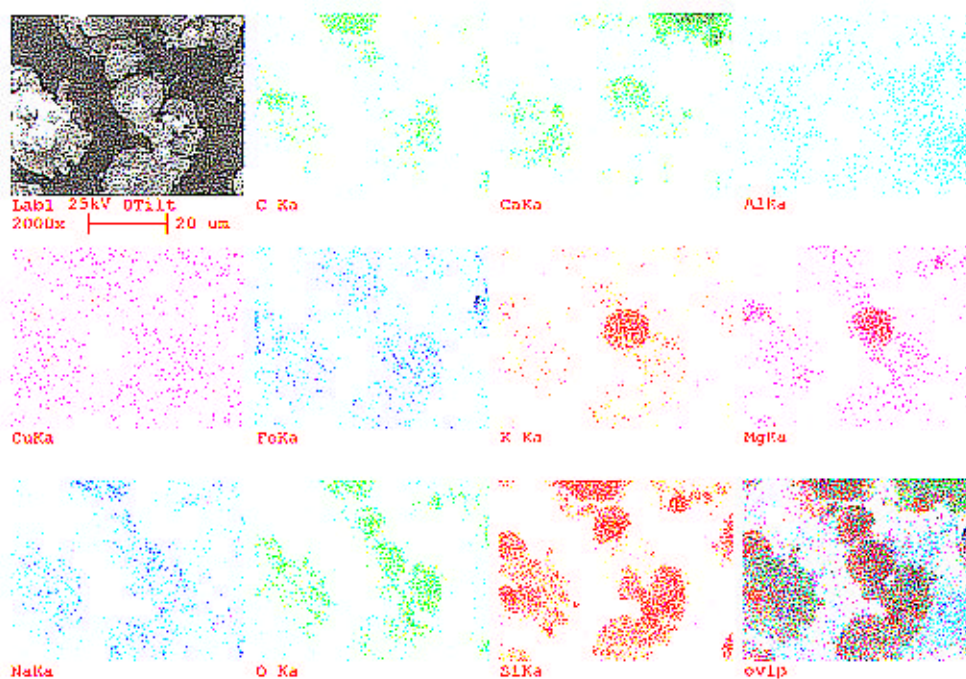


Figure 3. SEM image of the particulate material collected from the atmosphere with associated x-ray fluorescence analysis: SEM, Carbon, Calcium, Aluminum, Copper, Iron, Potassium, Magnesium, Sodium Oxygen, Silicon, and overlay of all measured elements.

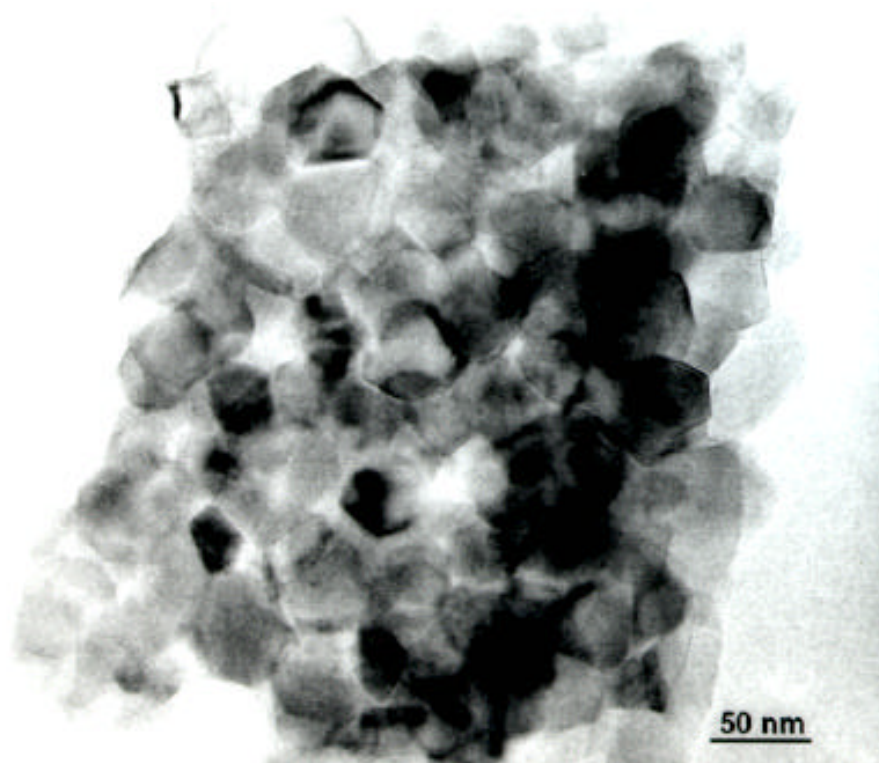


Figure 4a. High resolution image (at low magnification) of a dust particle.

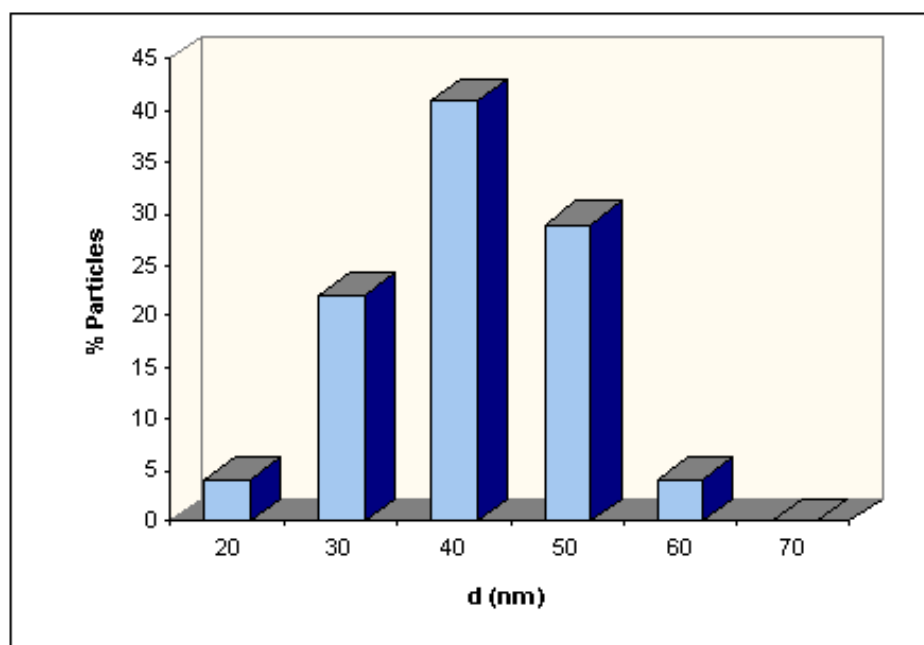


Figure 4b. Average particle size distribution of Fe_2O_3 nanoparticles in dust collected from the Mexico City Atmosphere

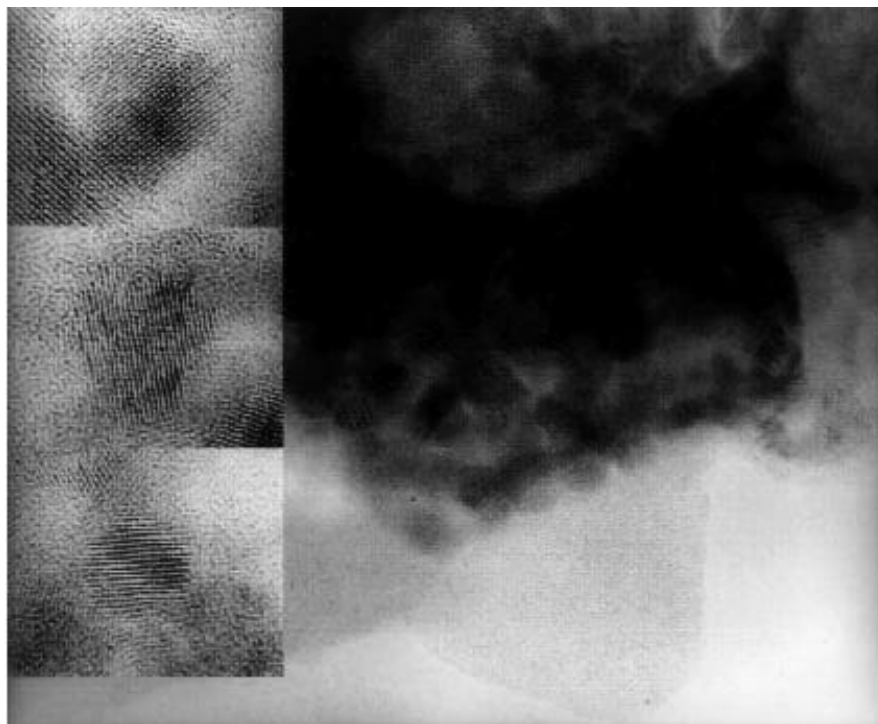


Figure 5a. High resolution image of a dust particle containing a clay with act as a support for nano-particles. The inset shows some high magnification of the Fe₂O₃ particles.

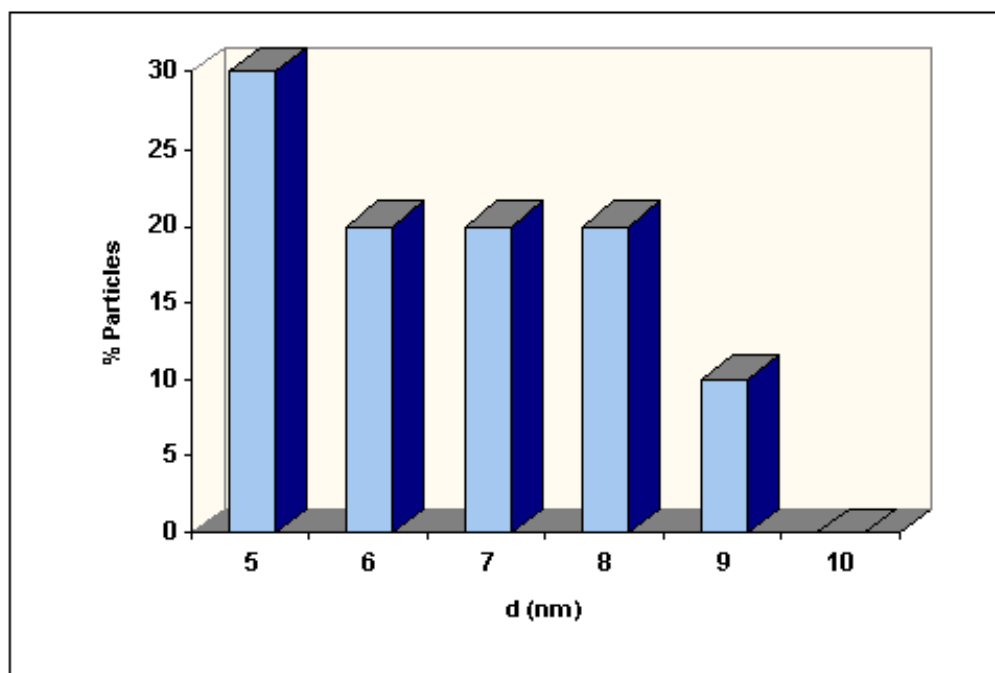


Figure 5b. Corresponding size distributions of the Fe₂O₃ particles.

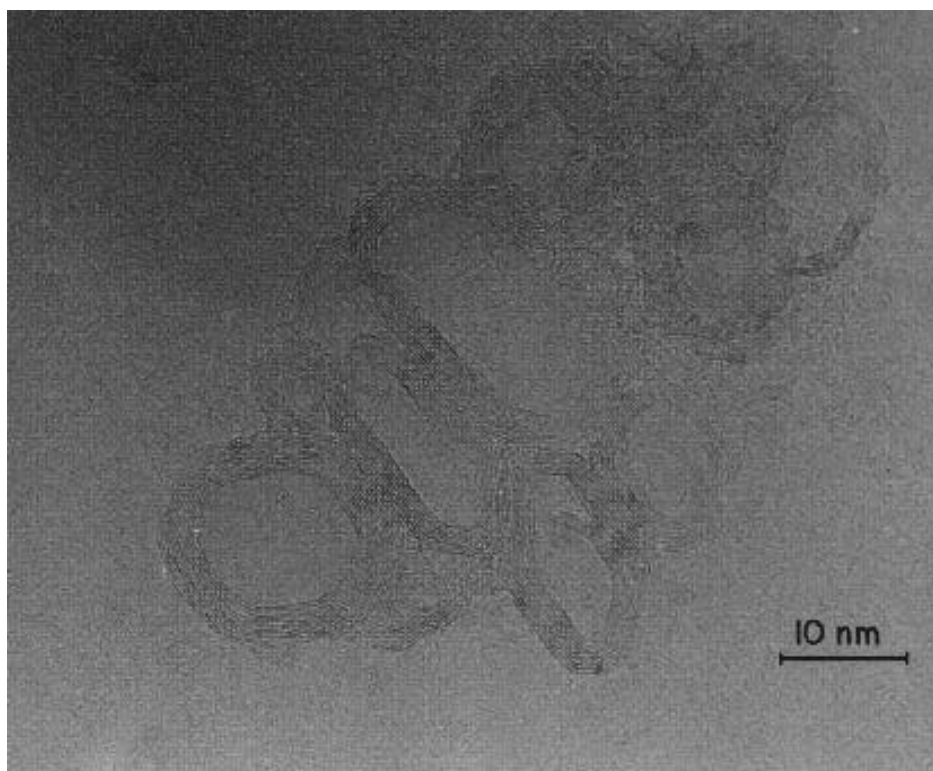


Figure 6. Fullerene cages formed in some soots observed in the sample of Nezahualcoyotl.