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Photocatalyzed oxidation of crude oil residue by beach sand

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Crude-oil residue in contact with beach sand and air was observed to undergo photocatalytic oxidation on exposure to light from a high pressure mercury vapor lamp. The kinetics of the heterogeneous reaction were of zero order in the mass of organic material present. Carbon dioxide was the oxidation product. No dark reaction occurred. The beach sand used contained magnetite and ilmenite as minor constituents. These materials are known to have catalytic properties for hydrocarbon oxidation. The results point to a "self-cleaning" process provided by the natural environment for the photocatalytic removal of crude-oil contamination from sandy beaches.

Keywords: Photocatalytic oxidation; catalytic oxidation of crude oil

1. Introduction

In an earlier publication [1] a preliminary report was presented on the photo-assisted oxidation of hydrocarbons in contact with sand. In the present paper we provide the details of the heterogeneous reaction kinetics, the identity of the metal oxides in beach sand responsible for the photocatalytic process, and an analysis of the potential contribution of the reaction for the removal of crude oil spills by oxidation to carbon dioxide.

Our inquiry concerns the photocatalytic properties of beach sand for the oxidation of organic materials. Typically, sand contains in admixture to silica the oxides of titanium, iron, calcium, aluminum, chromium, and magnesium [2]. Among these the titanium and iron compounds in the form of binary and ternary oxides are known to be catalytic and photocatalytic for various reactions.

For example, the Mar Chicita sands in Argentina are rich in ilmenite and hematite and have been used as catalysts [3]. Titania and titania-based perovskites are photocatalytically active for hydrocarbon oxidation [4–8].

2. Experimental details

As described in detail in ref. [1] a gas recirculating system with a total volume of 46 cm^3 was used in our studies It was made up of three major components: (1) a metal diaphragm gas pump, (2) a small cylindrical reactor (1 cm in diameter) made of Pyrex glass and provided with a horizontal glass frit for support of the sand particles, and (3) a glass manifold provided with a rubber septum for introduction of reactants and withdrawal of samples for gas chromatographic analysis with "Porapak S" as a column material at 375 K. At the beginning of each experiment the reactor was loaded with eight grams of sand and the system was flushed or filled with CO_2-free air (1200 Torr). For the blank experiments the sand was exposed for 3 hours to a continuous stream of air at 673 K in order to remove any oxidizable material. The flow velocity of the air inside the reactor was sufficient to agitate the sand. The sand particles had a geometric surface area of about 25 cm^2 g^{-1}, as measured by the BET method. The sand was exposed to radiation from a 200-Watt high pressure mercury vapor lamp. The light flux was 2.2×10^3 Watts m^{-2}, based on measurements with a photometer (Blak-Ray Model J-221) with wavelength sensitivity in the range from 300 to 400 nm. Using the same instrument the flux of solar radiation was determined to be 75 Watts m^{-2}. The light beam projected onto the sample was about 2 cm^2 in area. By means of appropriate glass filters the wavelength range of light striking the sample could be adjusted selectively (Corning filter #3384 with a cut-off limit of 480 nm, and #2404 with a cut-off limit of 620 nm).

A thermocouple (chromel-alumel), embedded in the sand measured its temperature during irradiation. To control the sample temperature a stream of air preheated to the desired temperature was blown continuously over the exterior of the reactor.

The photocatalyzed studies were performed with beach sand from Fort Funston, California. Its particle size distribution is listed in table 1. The sand contained two predominant types of crystals distinguishable by their color, one

Table 1
Size distribution of sand particles [a]

Sample	Size range (cm)	Mass fraction (wt%)	Color
A	0.025–0.050	51	brown
B	0.0007–0.025	32	brown/black
C	< 0.0007	17	black

[a] Sand from Fort Funston, California.

Table 2
Elemental analysis of beach sand [a]

Element	Sample fraction (wt%)	
	A[b]	C[c]
Si	80	40
Al	10	8.5
Fe	2.5	35
Ca	5.0	6.0
Mg	1.0	1.5
Ti	0.6	3.5
Cr	–	–
Na	1.0	–

[a] From Fort Funston, California, components are listed as oxides.
[b] Brown in color (see table 1).
[c] Black in color (see table 1).

light brown in appearance, the other black. The latter fraction exhibited ferromagnetic properties. Chemical analysis of the sand indicated the presence of the following elements in admixture to silica: Ti, Fe, Ca, Al, Mg, Na (table 2). X-ray diffraction studies (fig. 1) revealed the crystal phases of ilmenite ($FeTiO_3$) and magnetite (Fe_3O_4) as minor constituents. In addition, the sand contained a carbonaceous residue. Its chemical composition, deduced by infrared absorption analysis, indicated the presence of organic compounds commonly found in crude oil. The infrared spectra were obtained after pyridine extraction of the sand sample, folded by evaporation of the solvent and dissolution of the extract in chloroform. The spectra showed the presence of C-C and C-H bands in a wavelength region characteristic of hydrocarbon molecules (334 to 350 nm for C-H vibrations and 505 to 530 nm for C-C vibrations). The origin of the organic material in the sand is not known. Most likely the hydrocarbon residue was spilled at sea by some passing ship or oil tanker and subsequently was washed ashore and incorporated into the beach sand. The carbon content of the sand, determined by combustion analysis, amounted to 0.024 wt.% of the total sample.

3. Experimental results

In order to obtain a better understanding of the oxidation kinetics, the photocatalytic studies included the original beach sand and several samples of the same material subjected to different pretreatments, including (1) calcination by heating in flowing air at 670 K for 16 hours (sample blank), (2) washing in water and vacuum drying at 350 K, and (3) solvent extraction with pyridine followed by vacuum drying at 350 K.

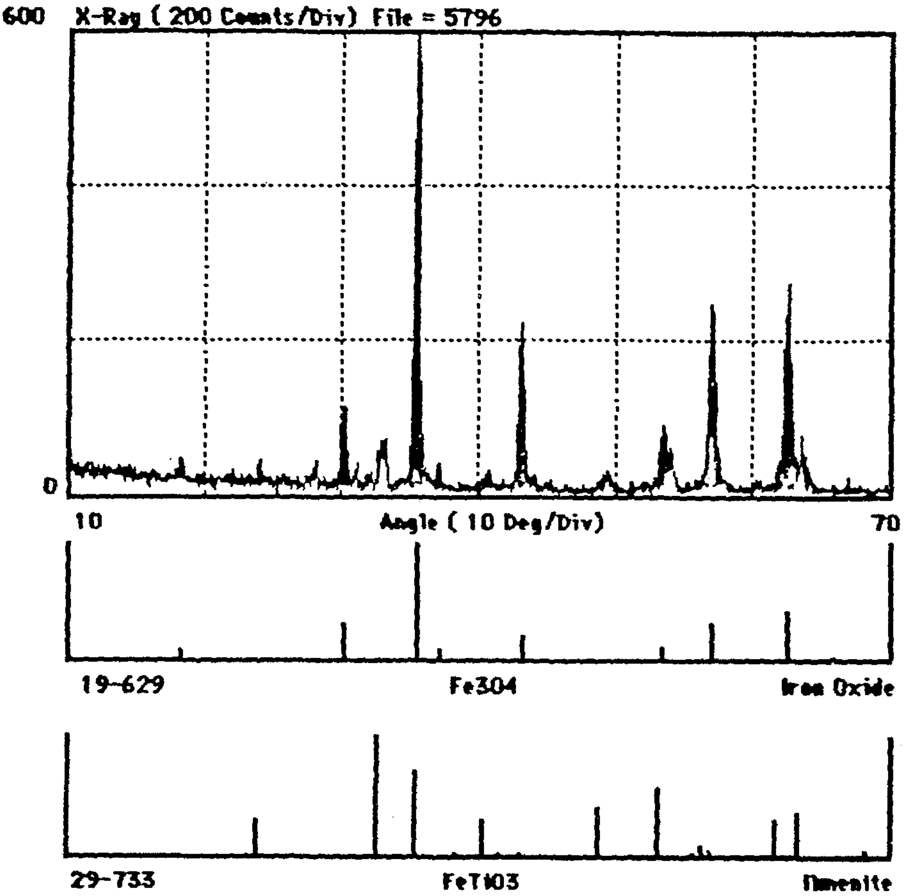

Fig. 1. X-ray diffraction analysis of beach sand from Fort Funston, California (referenced to magnetite and ilmenite).

The analysis of the oxidation-rate measurements was based on the rate of production of carbon dioxide for an irradiated sample area of 2×10^{-4} m^2 and a light flux of 2.2×10^{3} Watts m^{-2}. Within the limits of the analytical procedure no carbon monoxide was detectable as a product. The photocatalyzed oxidation of the hydrocarbon residue was observed to follow zero-order kinetics, i.e. the rate of CO_2 production was invariant with time and independent of the mass of hydrocarbon residue in the sample. At 325 K the photo-oxidation rate was found to be to 2.6×10^{-3} mol m^{-2} hr^{-1} (table 3,A). Since the measurements were carried out in the presence of a large excess of air, the reaction order with respect to O_2 is not established. Its concentration did not change significantly during the course of the experiment at the relatively low rates of conversion observed.

It is to be noted that exposure of the beach sand to a flowing stream of air for 16 hours at 673 K (sample blank) completely removed the hydrocarbon residue,

Table 3
Oxidation rate of hydrocarbon residue photocatalyzed by beach sand [a] at 325 K

Pretreatment	Rate [b] $(\mathrm{mol\ m^{-2}\ hr^{-1}}) \times 10^3$
(A) None	2.6
(B) Air at 673 K (16 hr)	0
(C) Water wash	2.6
(D) Pyridine solvent extraction	1.4
(E) Dark reaction	< 0.02

[a] From Fort Funston, California.
[b] Rate per unit of irradiated area of $(2 \times 10^{-4}\ \mathrm{m^2})$.

as evidenced by the absence of any CO_2 formation during subsequent exposure to air and irradiation (table 3,B). Also, water soluble materials in the sample did not contribute to CO_2 production, as demonstrated by the results obtained with a water-washed sample for which the rate was identical to that of the original one (table 3,C).

Only a fraction of the hydrocarbon residue was soluble in pyridine. After pyridine extraction and removal of the solvent by vacuum evaporation the rate of photocatalyzed oxidation was reduced by a factor of two relative to the untreated sample (table 3,D), indicative of the presence of residual oxidizable material in the sample.

In the absence of irradiation no CO_2 production was detected (table 3,E). In these experiments the temperature of the sample was maintained at 325 K, identical to that prevailing during illumination. The photocatalyzed oxidation rate of the residue was found to be dependent on the wavelength region of the light source. Exposure of the sample to light of less than 480 nm was much more effective for photooxidation than to higher wavelengths (table 4). Undoubtedly this effect is related to the photon energy required for the production of electronic carriers in the oxide semiconductor.

Table 4
Effect of wavelength on photo-oxidation rate [a]

Wavelength (nm)	Rate $(\mathrm{mol\ m^{-2}\ hr^{-1}}) \times 10^3$
all [b]	2.6
> 480	0.7
> 620	0.4

[a] Beach sand from Fort Funston, California.
[b] High pressure mercury vapor lamp.

4. Discussion

The composition of the beach sand employed in our studies points to a group of iron and titanium oxides as the most likely components for the photocatalytic reaction. Specifically, the complex oxides identified as ilmenite ($FeTiO_3$) and magnetite (Fe_3O_4) are capable to perform photocatalytic oxidation of hydrocarbons [7,8]. The ferromagnetic black phase of the sand was estimated to contain about 7 wt% magnetite and 0.7 wt% ilmenite, as deduced from X-ray diffraction studies. In general, the photocatalytic reaction on the surface of a photocatalyst is considered to involve first the production of electron (e^-)-hole (h^+) charge carriers by illumination of the semiconductor. As illustrated in the energy-band diagram (fig. 2), the charge carriers so generated can interact with adspecies located at suitable surface state energy levels associated with a reducing agent R, such as a hydrocarbon molecule:

$$R + h^+ \rightarrow R^+$$

or an oxidizing agent, such as O_2,

$$O_2 + 2e^- \rightarrow 2O^-.$$

The chemical nature of the surface oxygen species (O_2^-, O^-, $O^=$) involved in the oxidation process is not established, nor the mechanistic steps responsible for the formation of the intermediates and products. Since the formation of CO is not observed during the course of the photocatalytic reaction, its conversion to CO_2 must proceed more rapidly than that of its precursors. In the case of

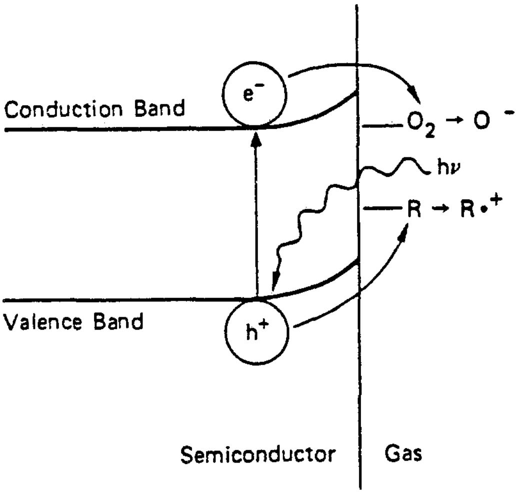

Fig. 2. Energy band diagram of semiconductor with photo-produced holes and electrons located at surface energy levels associated with oxygen and a reducing agent.

titania as a photocatalyst [9] the following steps have been proposed for CO oxidation:

$$\text{light} \rightarrow e^- + h^+ \tag{1}$$

$$CO + h^+ \rightarrow CO^+ \tag{2}$$

$$\tfrac{1}{2}O_2 + e^- \rightarrow O^- \tag{3}$$

$$CO^+ + O^- \rightarrow CO_2 \tag{4}$$

For continuous oxidation the photoproduced electrons are captured by oxygen at its surface state energy level located above the Fermi level of the semiconductor, and the holes by carbon monoxide, the reducing agent, at its surface state energy level positioned below the Fermi level. Interaction of the charged species by reaction (4) needs to be sufficiently rapid to prevent the formation of a space charge layer at the semiconductor surface. It is to be expected that by way of a similar mechanism the photocatalytic oxidation of organic compounds proceeds, such as those encountered in our study. However, this aspect requires further examination.

The significance of our research is to be found in the "self-cleaning" process provided by the natural environment for the removal of crude-oil contamination from sandy beaches by means of a photocatalytic process. Of interest is the fact that the oxidation proceeds at a significant rate at temperatures commonly prevailing at ocean beaches. In addition, the formation of carbon dioxide as the oxidation product of the complex organic compounds in the hydrocarbon residue provides an important pathway for reducing in magnitude one of the potential hazards of environmental pollution. Based on the results presented a simple calculation demonstrates the magnitude of the self-cleaning process to be expected with a solar flux of 75 Watts m^{-2} irradiating an area of 10^6 m^2 of contaminated beach sand. During an exposure of eight hours per day one obtains a contaminant removal rate of 700 mol per day, which is equivalent to about 100 kg per day of saturated hydrocarbon with an average molecular weight of 150. Thus, the elimination of 10^4 gallons of hydrocarbon contaminant would occur in less than six months.

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