

INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION



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SCHOOL ON PHYSIC IN INDUSTRY

27 January - 14 February 1986

" PHYSICS IN PETROLEUM INDUSTRY "

presented by

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These are preliminary lecture notes, intended for internal distribution to participants only.

PHASES IN THE PETROLEUM INDUSTRY

THERE ARE FIVE PHASES TO THE INDUSTRY:

- + EXPLORATION
- + PRODUCTION
- + TRANSPORTATION
- + REFINING
- + END USE

B.C. SUNDHOLM
10 FEBRUARY 1986

PROBLEMS HAVE HISTORICALLY BEEN VERY COMPLEX

- + EXPLORATION - Complicated geological structures
- Complex seismic data
- + PRODUCTION - Heterogeneous reservoirs
- Difficult flow modeling
- Organic-mineral interactions
- + TRANSPORTATION
- + REFINING - Complex, varied organic mixtures
- Little known about catalysis
- + END USE - Combustion under complex conditions

→ GREAT ADVANCES IN EXPERIMENTAL FACILITIES, THEORETICAL ANALYSIS HAVE MADE THESE PROBLEMS MORE TREATABLE

LECTURE PLAN

Introduction

- Scale of Energy Concerns
- Sources of Fossil Organics
- Exploration / Reserves

Physics of Exploration and Production

- Seismic Studies
- Other Topics: Gravitational Seismicity, Logistics
- Mechanistic Understanding: Fractal Modeling

Physics of Oil Refining

- Residuum Hydrocracking with Sulfide Catalysts
- Petroleum Refining with Noble Metal Catalysts
- Thermics of Catalytic Activity

Energy is a Major, Ever-Increasing Concern

WORLD ENERGY DEMAND



WORLD ENERGY SUPPLY



- Fast Growth of Demand
- Many Countries Face Fuel Shortages
- Oil a Crucial Component
- Fossil Fuels to Remain...

(See: World Energy Outlook - WEO)

Energy Comparison Tables

1 Quad = 10^{15} Btu's

- 172 MBoe as Oil
- 0.47 Trillion cubic feet of Natural gas
- 80 M Tons of Coal
- 2500 Tons of Uranium Oxide

World Ocean Depth and Shallow Seas and Hydrocarbon Generation

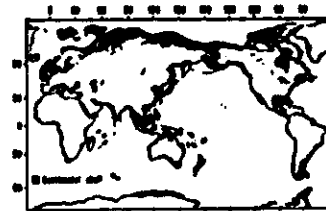


Fig. 1.1.1. Shallow seas of the world. Water depth in shallow seas is less than 200 m. Shaded areas show the location of shallow seas.



Fig. 1.1.2. Shallow seas of the world. Shaded areas show the location of shallow seas. Hydrocarbon generation is indicated by the shaded areas.

Table 1.1.1. Production of natural gas in the world (in 10⁹ m³)

Area	Area in km ² to 10 ⁶	Average production in 10 ⁹ m ³ per year	Total production in 10 ⁹ m ³ per year
Open ocean	120	50	6000
Coastal waters	50	100	5000
Deep-sea drilling	50	100	5000

(Table 1.1.1, p. 1.1)

Hydrocarbon Accumulation in Sediments (On a Geological Timescale)

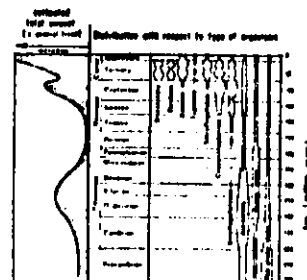
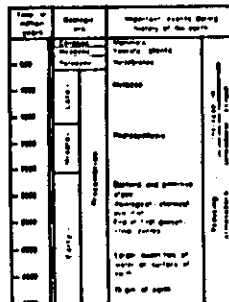


Fig. 1.1.1. Vertical distribution of hydrocarbon accumulation in sediments. The diagram shows the accumulation of oil and gas in different sedimentary basins over time.

• Less than 0.1% of Oceans are Reservoirs

(Table 1.1.1, p. 1.1)

Hydrocarbon Accumulation in Sediments

Sedimentary Basins



Types of Oil and Gas Accumulations



Although natural gas is found in all types of sedimentary basins, the most important gas accumulations are found in the sedimentary basins of oil and gas. The accumulation of oil and gas is controlled by the depth of the sediment column and the type of sedimentary basin.

(Table 1.1.1, p. 1.1)

ENERGY AND PETROLEUM CONSUMPTION

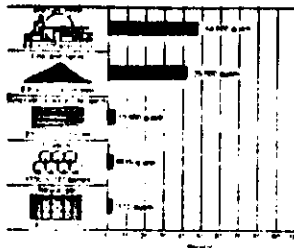


Figure 12.1
Remaining nonconventional world energy resources in 1980. The chart compares various energy sources: Coal, Oil, Natural Gas, Geothermal, Wind, Solar, and Hydropower. Coal is the most abundant, followed by oil and natural gas. Geothermal, wind, solar, and hydropower are shown in much smaller quantities.

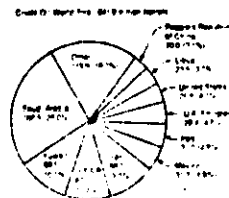


Figure 12.2
Distribution of world crude oil proved reserves in 1980. The chart shows the following percentages: Middle East (48%), North America (23%), Europe (13%), Asia (10%), Africa (7%), and Latin America (9%).

(Note: Source: "EIA")

OBSERVATIONS FROM SEVERAL SURVEY

- Large, but Finite Energy Reserves
 - Petroleum is Relatively Small Fraction
 - For Fills ~50% of our current energy needs
 - Process of Fossil Hydrocarbon Preservation is Delicate
 - Exploration is Increasingly More Complex
- ⇒ More Effective Use of Non-Petroleum Resources



Figure 14.1
World distribution of petroleum reserves in 1980. The chart shows the following percentages: Middle East (48%), North America (23%), Europe (13%), Asia (10%), Africa (7%), and Latin America (9%).

Figure 14.2
World distribution of petroleum reserves in 1980. The chart shows the following percentages: Middle East (48%), North America (23%), Europe (13%), Asia (10%), Africa (7%), and Latin America (9%).

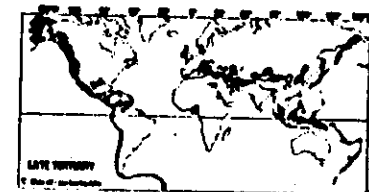


Figure 14.3
World distribution of petroleum reserves in 1980. The chart shows the following percentages: Middle East (48%), North America (23%), Europe (13%), Asia (10%), Africa (7%), and Latin America (9%).

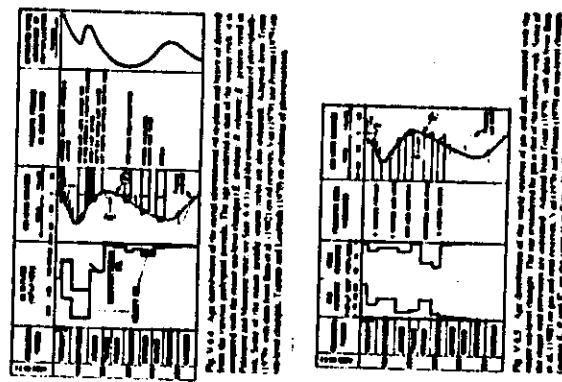


Figure 14.4
World distribution of petroleum reserves in 1980. The chart shows the following percentages: Middle East (48%), North America (23%), Europe (13%), Asia (10%), Africa (7%), and Latin America (9%).

Figure 14.5
World distribution of petroleum reserves in 1980. The chart shows the following percentages: Middle East (48%), North America (23%), Europe (13%), Asia (10%), Africa (7%), and Latin America (9%).

SOURCE OF OIL EXPLORATION

Dis. Source: Conf. 12, 1941, Conf. 1942

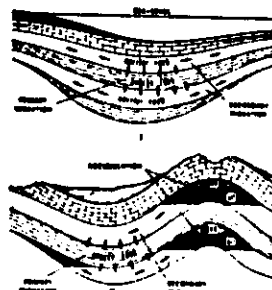


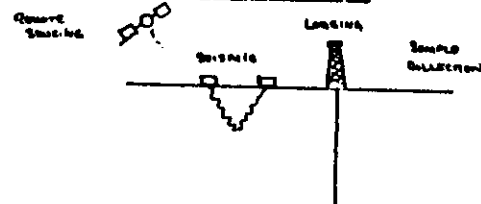
Fig. 11.1. Formation of oil and gas precursors: advanced generation of primers and secondary migration to the source and advanced stage of biodegradation / burial phase of primers and secondary migration // Advanced stage of primers and secondary migration and biodegradation of biodegradation.



Fig. 11-5. Same procedures for ex' given interrupted with one plug (disturbed after 10-15 min. for 1).

(Trent & White, 1983)

SEVERAL SOURCES OF GEOLOGICAL INFORMATION



- * Remote Sensing
 - Spectral Reflectance
 - Spectral Emittance
 - Thermal Inertia
 - Radar
- * Sample Extraction
 - Organic & Mineral Analysis

* Gerre and Rowan Statute 21, 481 (1901)

•• Tisor & Welter, Ger

STRESSING FOR SMOKE RESCUE SURVIVORS.

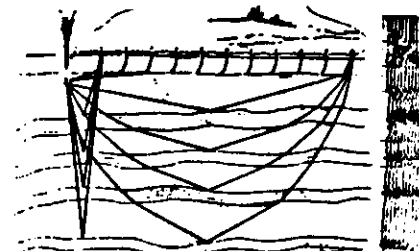
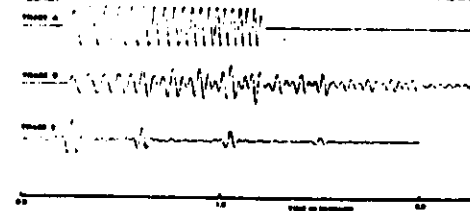


Fig. 5. Geometry of reflection from a dielectric medium coated on a refractory mirror. From a to b the corresponding input signal. Trace B is the signal that would be recorded for a reflecting medium. Δ is the difference of wave a and b signals at time t . Δ corresponds to the time delay between reflection stages in four pulses and for each

Fig. 1. Scheme of the optical system method. A stage equipped with a high precision micrometer screw which can adjust the interference distance and focus. The reference air flowing on the surface and the sample displaced and recorded the light in a micrograph. Step 10 detector detects of appropriate optical distance from the flow tube. The image each 4 seconds. Measurements are every other used to be up to 100 hours.



(L. 1014, August
Teacher 20, 1978)

Scientific Policy Summary



Fig 1. A large, well-developed fibrous root of a young *Quercus* seedling. The root is shown in cross-section, revealing the internal structure of the root tip. The root is approximately 1 cm in diameter and is covered in a dense, fibrous network of root hairs. The root tip is clearly visible, showing the characteristic shape of a young root.

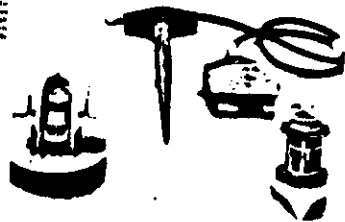


It is a device capable of being in various configurations. A system of organs that organ is designed to a specific shape and in case of their number is altered by the same (the work with the detector with

(Latin)

Seismic Detectors (Geophones)

Fig. 1. Typical geophone for seismic measurements. It consists of a coil of wire mounted on a base, with a permanent magnet attached to the coil. The coil is connected to an amplifier, and the magnet is connected to a recording device. The geophone is used to measure the acceleration of the ground during an earthquake.



(Levin)

Data Collection and Analysis Strategy

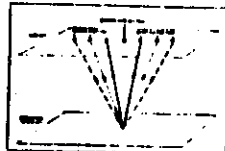
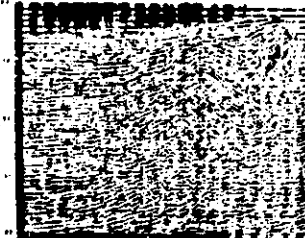


Fig. 2. Scheme of a method of selecting seismic stations. The diagram shows a network of stations (represented by dots) connected by lines, with a central point labeled 'STATION'.

Fig. 3. Typical seismic data. The diagram shows a series of seismic waveforms (represented by lines) recorded at different stations. The waveforms are labeled with station names and times.



(Levin)

Well Logging - Physical Properties Down The Well

- + ELECTRICAL
- + NUCLEAR
- + SONIC

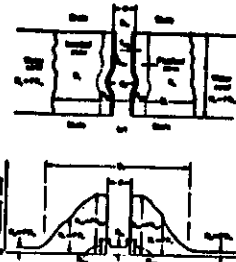
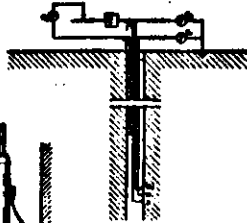


Fig. 3. Well log and location diagram. The diagram shows a well log (represented by a vertical line) and a location diagram (represented by a map) showing the well's location relative to a seismic station.

- + Complex Environment
 - + Correlation Based
 - + Evolving Geologic Situation
- (Dr. Victor "Gus" G. 1961)

Electrical Log From Seismic Records

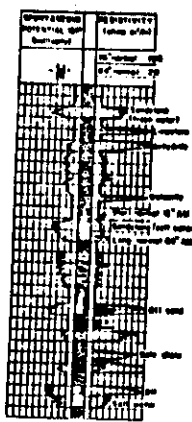


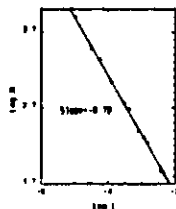
Figure 1.12. Diagram showing how electric log data is used to calculate porosity. The diagram shows a well log with electrical log data and a corresponding porosity log.

Figure 1.13

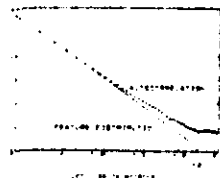
Typical electric log, showing the SP curve at the top, a multiple sample log in the center, and the resistivity log at the right. (Adapted from Seismic and Log. "Electric Logging" in E. W. Fisk and J. H. Fisk, Geologic Methods, 2nd ed., McGraw-Hill, 1951, p. 235, Fig. 132)

(Dr. Lawrence, Geology of Petroleum, 1967)

SANDSTONE STRUCTURES CAN BE DESCRIBED BY FRACTALS



943 | A log-log plot of the number of geometric
fractals of size λ per unit length of the wire l for various
values of λ for various conditions.



4.2 It is the site of the pure zone directly underlying
the zone taken on a quartz cemented sandstone from
the top. The shape of the straight line was taken from
the zone distribution collected on a fracture surface
to 1. The measurements were taken by optical
microscopy on 5000 images of polished rock thin sections.
The results of measurements are shown in the figure.

TABLE 1 Results of SEM measurements on various specimens

Sample	Percent Distillate	g/lpm	Calculated	Measured
Tight gas seal dist.	3.57	25	67	53-58
Tight gas seal atmos.	3.50	6	76	60-76
Carbamide	2.70	90	10	11-12*
Methyl	3.01	90	14	16.0
St. Peter's	3.07	50	3*	30-39

(Kato and Thompson, Rep. Law Lib. 24, 255
(1955))

THE FLUORESCENT GROWTH OF VIBRIO FUSUS

- Provides Warm Thresh & Fluid of
Blood Vessels
- Particularly Important for
Secondary and Tertiary Oil
Recovery

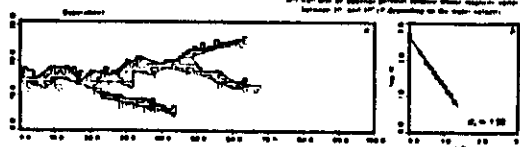
[illegible]

Fig. 2. Schematic representation of the distribution of δ from experimental data of Fig. 1. a) Diagram of how the average length of the damaged super is measured with a ruler of length $l_0 = 5$ b) The shape of the average line $m = \delta$. δ from which $m = \delta$ and $\delta = 1$ is

ഇതുപ്രകാരം:

- Exploration And Production Are Formidable:
 - Heterogeneous Structures
 - Complex, Multiphase Interactions
 - Need For High Spatial Resolution

- Current Computational, Experimental, Theoretical Developments Hold Great Promise for Quantitative Advances
 - Supercomputing
 - High Sensitivity Spectroscopy
 - New Theoretical Approaches: Fractals

PHYSICS OF PETROLEUM REFINING

GENERAL OBJECTIVES:

- COMPONENT SEPARATION
- MINERAL / METALS REMOVAL
- HYDROGEN (NITROGEN, SULFUR) REMOVAL
- MOLECULAR WEIGHT REDUCTION
- BLENDING / PRODUCT FORMULATION

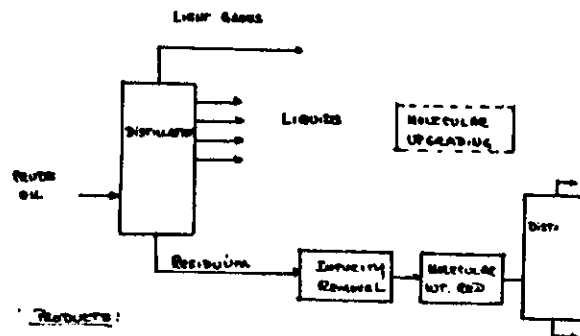
AND DONE BY A COMBINATION OF PHYSICS (SEPARATIONS)
AND CHEMISTRY (CONVERSION)

REFINING CONVERSIONS ARE ACCOMPLISHED BY SEVERAL METHODS

- + THERMAL TREATMENTS
- + CATALYSIS (HOMOGENEOUS OR HETEROGENEOUS)
 - MINERALS (CLAYS, ZEOLITES, ...)
 - METALS (TRANSITION METALS, NOBLE METALS, ALUMINUM)
 - OTHERS (SULFIDES, OXIDES)

(DR. G.M. STRECHT, 'HETEROGENEOUS CATALYSIS IN
PETROLEUM', MC GRAW-HILL, 1966)

GENERAL REFINING STRATEGY

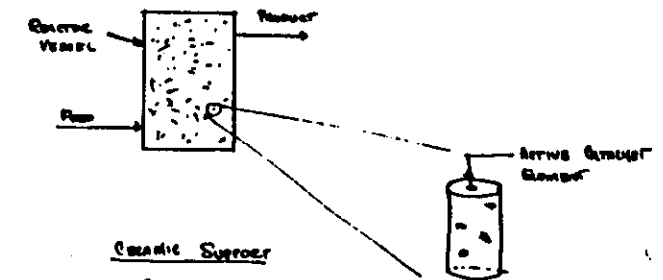


PRODUCTS:

- + CHEMICAL FEEDSTOCKS / FEEDSTOCKS
- + FUELS (GASOLINE, KEROSENE, FUEL OILS, ...)
- + LUBRICANTS
- + HEAVY PRODUCTS (ASPHALT, ...)

(THE PETROLEUM HANDBOOK, ELSEVIER, 1955)

HETEROGENEOUS CATALYSIS: A SCHEMATIC



Catalytic Support

- Pore Volume
- Pore Size Distribution
- Mechanical Properties

HYDROTREATING CATALYSIS: A SPECIFIC EXAMPLE

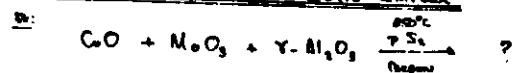
GOAL: TO UPGRADE CRUDE OILS AND RESIDUA (350-550°C)

	KUWAIT	BRABANT HEAVY	ARABIAN HEAVY
Sulfur (wt.%)	4.21	8.72	4.31
Vanadium (ppm)	58	145	98
Nickel (ppm)	12.7	88.6	26.9
C ₄ AROMATICS (wt.%)	3.7	8.6	6.5
Refr. Carbon (wt.%)	9.8	10.0	13.1

- GOALS:
- DEWAXILLIZATION
 - METALLOID REMOVAL (S & N)
 - MOLECULAR WEIGHT REDUCTION

(See, CATALYST DEACTIVATION 6 (Elsevier, 1980) p. 522)

THE OPERATING CATALYST IS QUITE COMPLEX



- MOLYBDENUM OXIDES / SULFIDES
- COBALT "PROMOTER" (RELATIONSHIP TO Ni?)
- ALUMINA SUPPORT EFFECTS
- DEPOSITED CARBON
- DEPOSITED METALS (V, Ni, ...)

⇒ CAN ONE DEFINE CATALYSIS?

- + MOLECULAR MECHANISMS?
- + ACTIVE SITES?

MoS₂ IS ONE OF A LARGE CLASS OF LAYERED SULFIDES

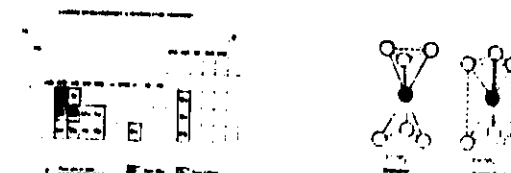


Fig. 1. The structure of layered disulfides.

- + SUPERCONDUCTORS, SEMICONDUCTORS, METALS
- + NON-STOICHIOMETRY
- + INTERCALATION

(See, BLANCHARD, Rev. Sci. (1984) 21, 281 (1987))

MODEL REACTIONS TEST CATALYSTS

EXAMPLE: DIBENZOTHIOPHENE DERIVATIZATION

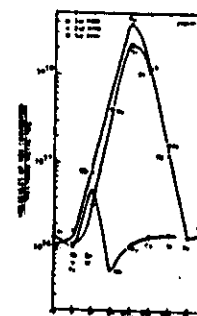


Fig. 2. Effect of temperature on the rate of dibenzothiophene conversion.

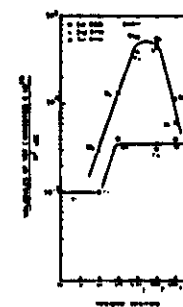


Fig. 3. Effect of catalyst concentration on the rate of dibenzothiophene conversion.

Notes: ELECTRONIC, GEOMETRIC, CHEMICAL

(See, BLANCHARD, Rev. Sci. (1984) 21, 281 (1987))

RELATION TO BULK PHYSICAL PROPERTIES

Rate of Reaction

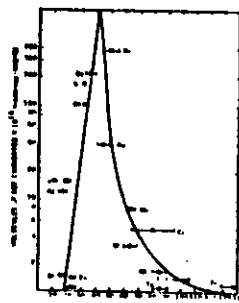


FIG. 1. Rate of Reaction of H_2O_2 on Fe^{2+} activity.

PERCENT T.M. D ELECTRONIC SPECTROSCOPY

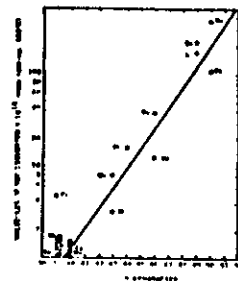


FIG. 2. Plotting of D.E. phenomena for the transition spectra on Fe^{2+} activity.

(CHAMBERLAIN)

Activity Suppression of Track Electronic Band Properties

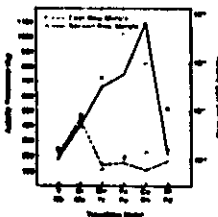


FIG. 3. Activity suppression of track electronic properties.



FIG. 4. Relative energies levels for various spin densities.

(CHAMBERLAIN)

Oxygen Adsorption, Surface Area of Fe_2O_3 , TRACK LBS ACTIVITY

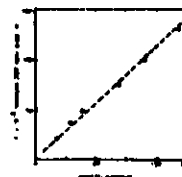


FIG. 11. Oxygen adsorption on surface area for Fe_2O_3 activity.



FIG. 12. Surface area on track activity for Fe_2O_3 activity.

- Extracted Result
- Fe_2O_3 has a specific structure - Not Layered

(CHAMBERLAIN)

Aluminum Suppression of O. Adsorption and ESR for Fe_2O_3

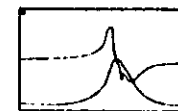
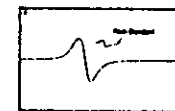
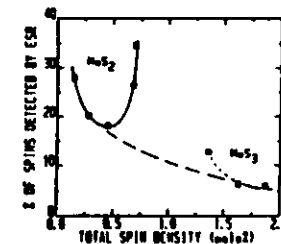
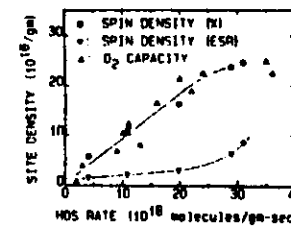


FIG. 13. ESR spectra of Fe_2O_3 with varying Al_2O_3 content. The spectra were recorded on a Varian A-10 ESR spectrometer. The Fe_2O_3 was prepared by the thermal decomposition of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at 500°C for 24 hours. The Al_2O_3 was prepared by the thermal decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at 500°C for 24 hours. The Fe_2O_3 and Al_2O_3 were mixed in a 1:1 ratio and the mixture was calcined at 500°C for 24 hours.

(CHAMBERLAIN)

SAME AREA DOES NOT TRACK MOS ACTIVITY FOR MOS

- MOS activity does track
- O_2 adsorption and
- Mo^{5+} donor density from electronic spin resonance

Suggests edge sites are active

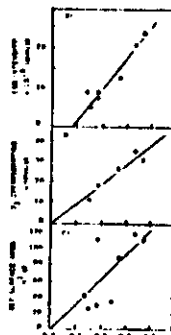


Fig. 1. MOS activity vs. O_2 adsorption, Mo^{5+} donor density, and electronic spin resonance signal.

(Lichtenhan, Pomeroy, Kinsman, J. Electrochem. Soc., 115, 1055 (1968))

Electron Microscopy of MoS_3 Oxidation



Fig. 2. Electron micrograph of MoS_3 after oxidation showing surface morphology.



Fig. 3. Schematic diagram of the stages of MoS_3 oxidation.

Fig. 4. Schematic diagram of the stages of MoS_3 oxidation.

Thermodynamic reaction for MoS_3 in three oxide-sulfide systems

(Lichtenhan, Pomeroy, Kinsman, J. Electrochem. Soc., 115, 1055 (1968))

Electron Microscopy of MoS_3 Oxidation

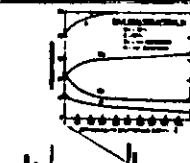


Fig. 5. Electron micrograph of MoS_3 after oxidation.

Fig. 6. Electron micrograph of MoS_3 after oxidation.

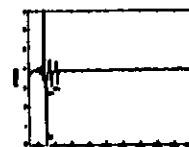


Fig. 7. MOS activity vs. O_2 adsorption, Mo^{5+} donor density, and electronic spin resonance signal.

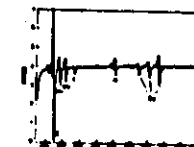


Fig. 8. MOS activity vs. O_2 adsorption, Mo^{5+} donor density, and electronic spin resonance signal.

(Lichtenhan, Pomeroy, Kinsman, J. Electrochem. Soc., 115, 1055 (1968))

MoS_3 Surface Oxidation in Aqueous MoS_3

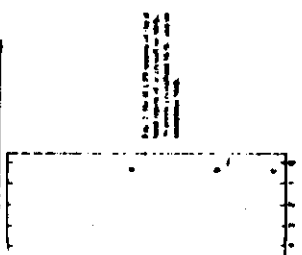


Fig. 9. Electron micrograph of MoS_3 after oxidation.

Fig. 10. Electron micrograph of MoS_3 after oxidation.

(Lichtenhan, Pomeroy, Kinsman, J. Electrochem. Soc., 115, 1055 (1968))

ANALYTICAL SPECTROSCOPY DISCLOSES CRYSTAL SITES ON CATALYSTS



FIG. 1. Schematic representation of the different phases present in a typical catalyst support structure.

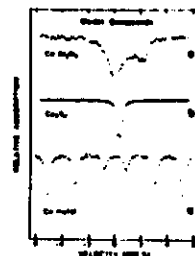


FIG. 2. X-ray fluorescence spectra of catalyst support phases. (a) oxide, (b) Co-Mn-S, (c) Co-Mn, (d) Co-Mn-S. (Figure adapted from Ref. 1.)

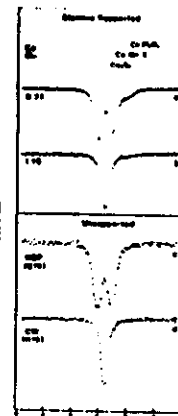


FIG. 3. X-ray fluorescence spectra of catalyst support phases. (a) oxide, (b) Co-Mn-S, (c) Co-Mn, (d) Co-Mn-S. (Figure adapted from Ref. 1.)

(TOSHIKI I. CHANON, FOR. REV. SCI. IND. 26, 395 (1969))

ABSORPTION AND SURFACE PROPERTIES OF Co-Mn-S CATALYSTS

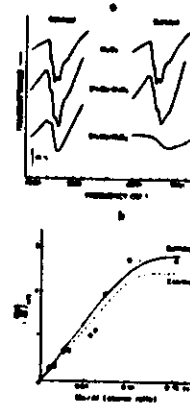


FIG. 4. (a) Absorption spectra of catalyst support phases. (b) Surface area of catalyst support phases. (Figure adapted from Ref. 1.)



FIG. 5. (a) Absorption spectra of catalyst support phases. (b) Surface area of catalyst support phases. (Figure adapted from Ref. 1.)

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CATALYTIC ACTIVITY TRACKS AMOUNT OF Co-Mn-S PHASE

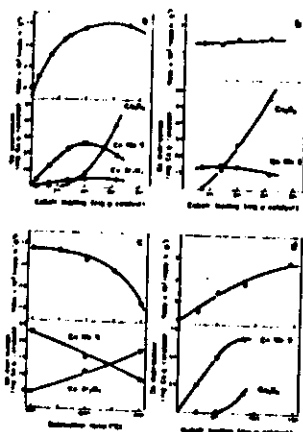


FIG. 6. Catalytic activity tracks amount of Co-Mn-S phase. (Figure adapted from Ref. 1.)

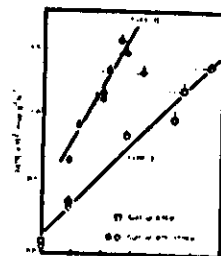


FIG. 7. Catalytic activity tracks amount of Co-Mn-S phase. (Figure adapted from Ref. 1.)

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EXAFS MEASUREMENTS SUGGEST SMALL Co-Mn-S CRYSTALLITES ON CATALYSTS

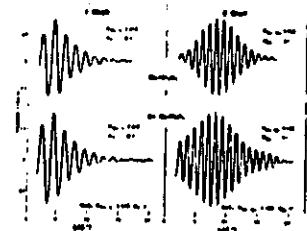


FIG. 8. EXAFS measurements suggest small Co-Mn-S crystallites on catalysts. (Figure adapted from Ref. 1.)

- $\sim 10\text{\AA}$
- EXISTENCE OF CRYSTAL FEATURES THE Co-Mn-S PHASE
- Co-Mn-S PHASE IS THE CRYSTALLITE PHASE



FIG. 9. Schematic diagram of Co-Mn-S crystallite structure. (Figure adapted from Ref. 1.)

(TOSHIKI I. CHANON)

Optimal Existence and Characterization is the Key
to Understanding Catalysis

- Molecular Conversion Processes
 - Products
 - Kinetics
 - Catalyst Chemistry Variations
 - Battery of Characterization Techniques
 - ESR
 - NMR
 - NMR
 - Microscopy, Microprobe
 - EXAFS
 - Magnetic Susceptibility
 - UPS, XPS
- In Situ
- Molecular Adsorption —
 - Theoretical Self Consistency

