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

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SCHOOL ON PHYSIC IN INDUSTRY

27 January - 14 February 1986

" PHYSICS IN PETROLEUM INDUSTRY "

presented by

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Physics in the Petroleum Industry

There are five phases to the industry:

- ✦ Exploration
- ✦ Production
- ✦ Transportation
- ✦ Refining
- ✦ End Use

B.G. Silbernagel
10 February 1986

Lecture Plan

Introduction

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

Physics of Exploration and Production

- Seismic Studies
- Other Probes: Remote Sensing, Logging
- Microscopic Understanding: Fractal Modeling

Physics of Oil Refining

- Residuum Hydroconversion with Sulfide Catalysts
- Petroleum Reforming with Noble Metal Catalysts
- Theories of Catalytic Activity

Problems Have Historically Been Very Complex

✦ Exploration
- Complicated geological structures
- Complex seismic data

✦ Production
- Heterogeneous reservoirs
- Difficult flow modeling
- Organic-mineral interactions

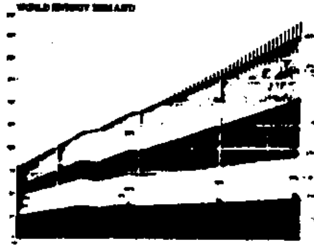
✦ Transportation

✦ Refining
- Complex, varied organic mixtures
- Little known about catalysis

✦ End Use
- Combustion under complex conditions

⇒ Recent advances in experimental capabilities, theoretical analyses make these problems more tractable

Energy is a Major, Worldwide Concern



- [illegible]
- [illegible]
- [illegible]
- [illegible]

([illegible])

1

Energy Conversion Factors

1 Quad = 10^{15} BTU's

= 172 Mbbls of Oil

= 0.97 Trillion cubic feet of Natural gas

= 50 M Tons of Coal

= 2500 Tons of Uranium Oxide

Major Shelf Areas and Shallow Seas Favor Hydrocarbon Generation

[illegible]

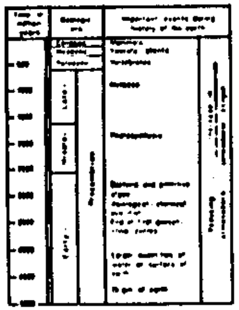
Area	[illegible]	[illegible]	[illegible]
Open ocean	[illegible]	[illegible]	[illegible]
Coastal waters	[illegible]	[illegible]	[illegible]
Areas with upwelling	[illegible]	[illegible]	[illegible]

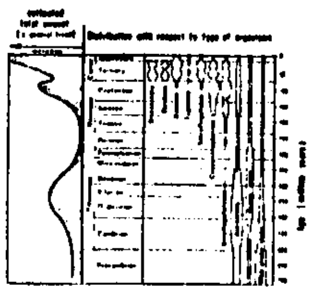
[illegible]

(Tissot & Welte, [illegible])

Major Hydrocarbon Accumulations in Geologic Record

(On a Geological Timescale!)





[illegible]

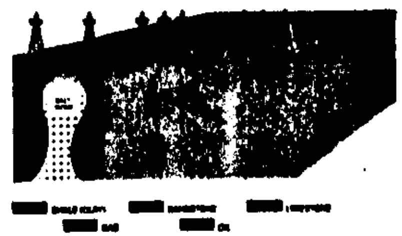
- Less than 0.1 % of Organics are Preserved

(Tissot & Welte, [illegible])

Hydrocarbons Accumulate in Sediments

Sedimentary Basin

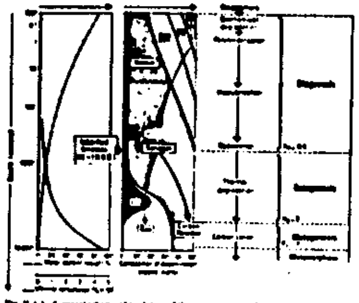
Types of Oil and Gas Accumulations

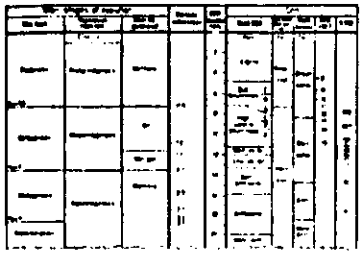


[illegible]

([illegible] 'How Does Oil & Gas' [illegible])

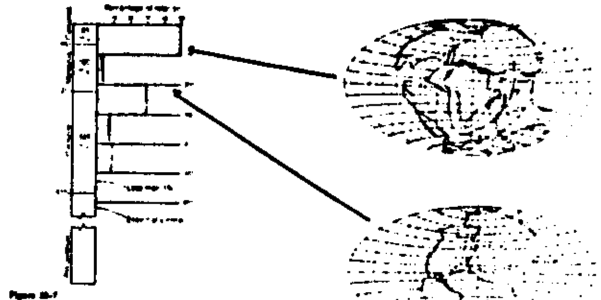
Heat Associated with Burial Matures Kerogens



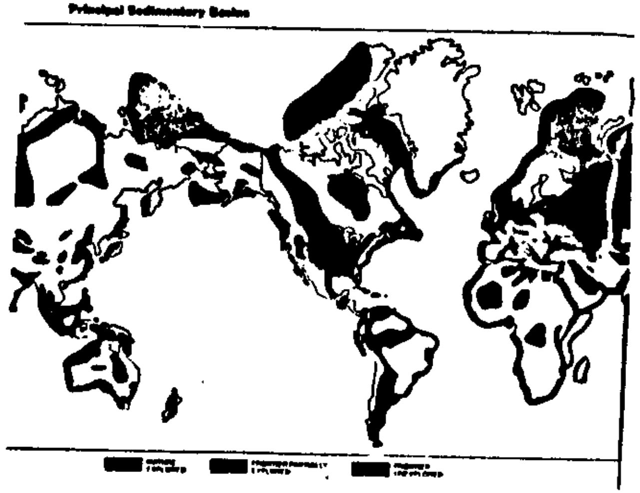


(Tissot & Welte)

[illegible] Oil [illegible]

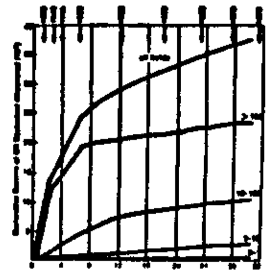


Principal Sedimentary Basins



(Source: "[illegible] Oil & Gas" [illegible])

Patterns of Drilling and Oil Discovery

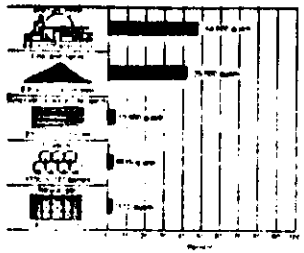


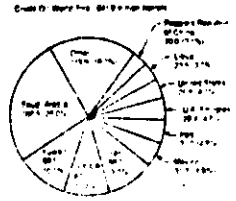
Reason:

Largest Fields Underlie Large Surface Areas

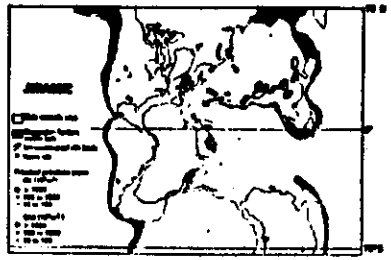
([illegible], American Scientist [illegible])

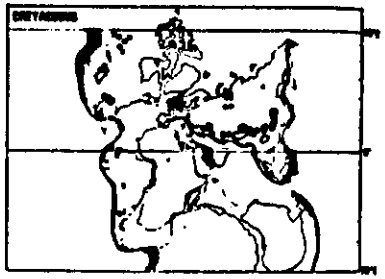
Energy and Petroleum Geology





(Photo (Session : "Earth")

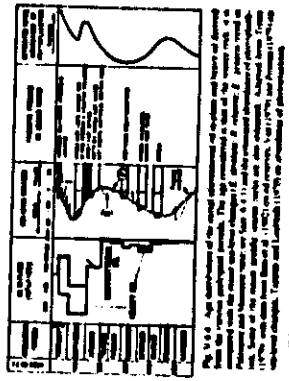


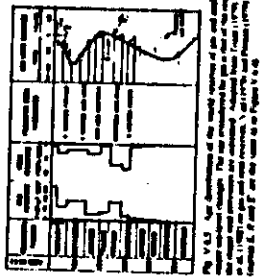


Observations from Regional Surveys

- Large, But Finite Energy Resources
- Petroleum a Relatively Small Fraction
  - for Fuels ~80% of Our Current Energy Needs
- Process of Fossil Hydrocarbon Preservation is Delicate
- Exploration is Becoming Ever More Complex

⇒ More Effective Use of Non-Petroleum Resources





Stages of Oil Exploration

Oil Sources: Coal vs. Ideal Case

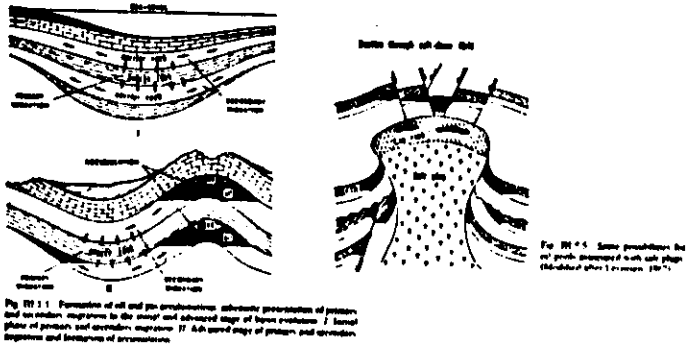
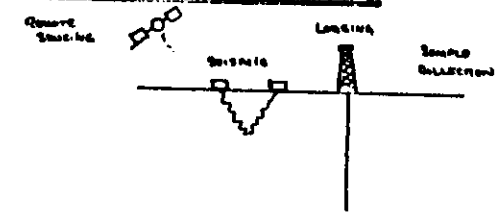


Fig. III.11 Formation of oil and gas accumulations: schematic presentation of primary and secondary migrations in the early and advanced stage of basin evolution. I Normal phase of primary and secondary migration. II Advanced stage of primary and secondary migrations and formations of accumulations.

(Tissot & Welte, Pt. 3)

Several Sources of Geological Information



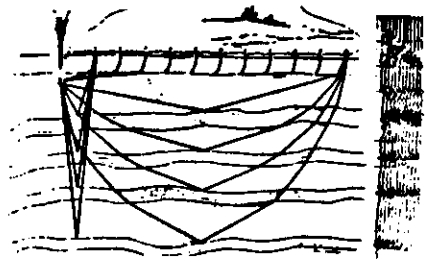
* Remote Sensing
  - Spectral Reflectance
  - Spectral Emittance
  - Thermal Inertia
  - Radar

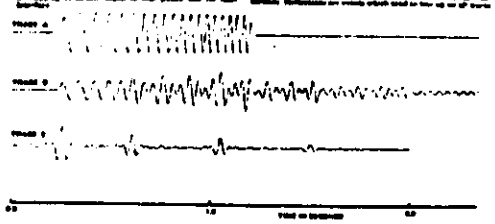
** Sample Extraction
  - Organic & Mineral Analysis

* Goetz and Rowan Science 211, 781 (1981)

** Tissot & Welte, Ref

Principles of Seismic Reflection Surveys



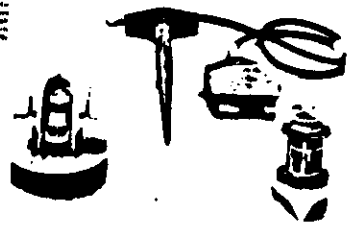


(Levin, Physics Teacher 19, 19 (1981))

Seismic Energy Sources

(Levin)

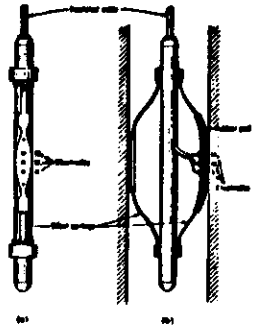
Seismic Detectors (Geophones)

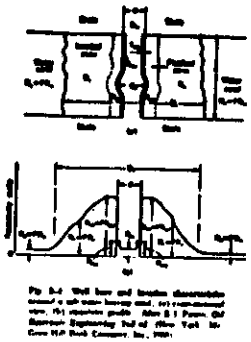


(Levin)

Well Logging — Physical Properties Down the Well

+ Electrical
+ Nuclear
+ Sonic

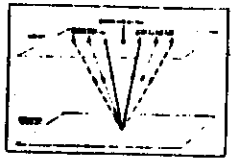


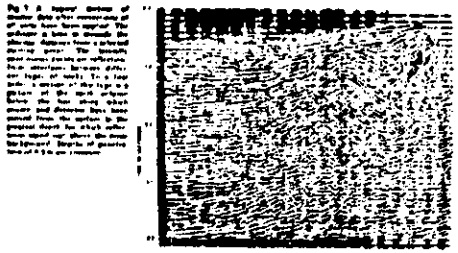


- Complex Environment
- Correlation Based
- Extensive Computer Simulation

(See Pickett "Fundamentals of Well Log Analysis" - 1967)

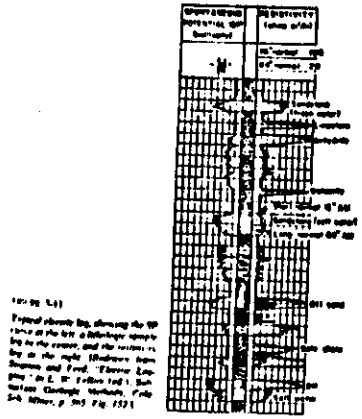
Data Collection and Analysis Strategy





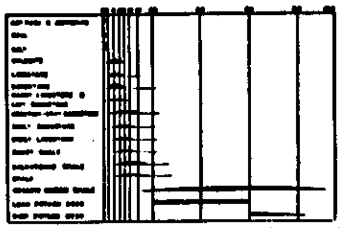
(Levin)

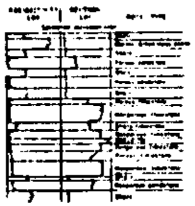
Electrical Logs Show Formation Thickness



(See Levorsen, Geology of Petroleum, Freeman, 1967)

Gamma Ray / Neutron Logs Sense Sediments, Water





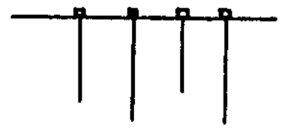
Principal Radioactive
Elements: U, Th, ^{40}K

$\gamma \sim 1-2$ MeV

(Ref. Levorsen)

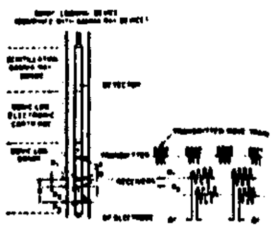
Production of Dispersed Oil is a Challenge

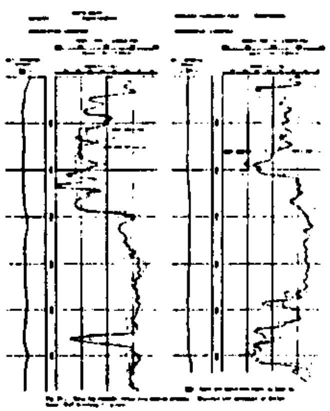
- Optimum Rate of Withdrawal
- Optimum Placement of Wells
- Secondary, Tertiary Methods
- Maintaining Oil Flow
- Capillary Forces
- Oil - Mineral Interactions



⇒ Goal: A Microscopic Understanding of Fluid Flow in Rocks.

Sonic Logs Sense Porosity, Mineral Properties





(Ref. Pirson - "Handbook of Well Log Analysis", 1961)

Powerful New Means for Analyzing Porous Media, Percolation, Aggregation: Fractals

- Complex Dimensionality: - String in a Plane, Crumpled Paper

Dilation Symmetry: If $N(\lambda R) = \lambda^D N(R)$,

Taking $\lambda = 1/R$, $N(R) = N(1) R^D$

D: Hausdorff Dimension

For the density of points between R & R+dR: $= g(R)dR$

$$R^{d-1} g(R) \sim R^{D-1}$$

$$\therefore g(R) \sim \frac{\text{Const.}}{R^{d-D}}$$

Self Similarity — A Part of the System Contains All Information of the Whole.

— Limited Range of Application

Sandstone Structures Can Be Described By Fractals

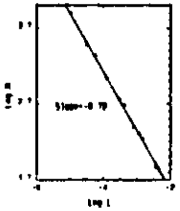


FIG. 1. [illegible]

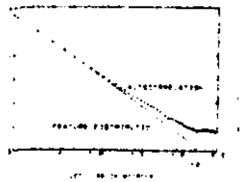


FIG. 2. [illegible]

TABLE I. Results of SEM measurements on various sandstones

Sample	Fractal dimension	l_1 (µm)	Porosity (%) Calculated	Porosity (%) Measured
Tight gas sand [illegible]	2.57	2.5	4.7	5.3–5.8
Tight gas sand [illegible]	2.68	6	7.6	6.9–7.6
Coconino	2.79	40	18	11–12
Navajo	2.81	90	14	16.0
St. Peter's	2.87	50	2?	20–29

(Katz and Thompson, Phys. Rev. Lett. 54, 1325 (1985))

The Fractal Growth of Viscous Fingers

- Pushing Water Through A Fluid of Higher Viscosity
- Particularly Important For Secondary and Tertiary Oil Recovery

FIG. 1. [illegible]

(Nittmann, Daccord, and Stanley, Nature 314, 141 (1985))

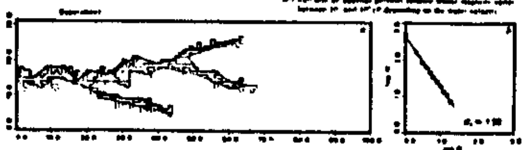


FIG. 2. [illegible]

Conclusions:

- 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

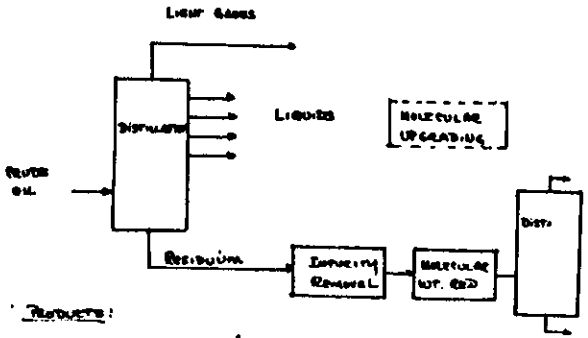
Physics of Petroleum Refining

General Objectives:

- Component Separation
- Mineral / Metals Removal
- Heteroatom (Nitrogen, Sulfur) Removal
- Molecular Weight Reduction
- Blending / Product Formulation

⇒ Done By A Combination of Physics (Separations) and Chemistry (Conversion)

General Refining Strategy



Products:

+ Chemical Feedstocks / Chemicals
+ Fuels (Gasoline, Kerosene, Fuel Oils, ...)
+ Lubricants
+ Heavy Products (Asphalt, ...)

(The Petroleum Handbook, Elsevier, 1983)

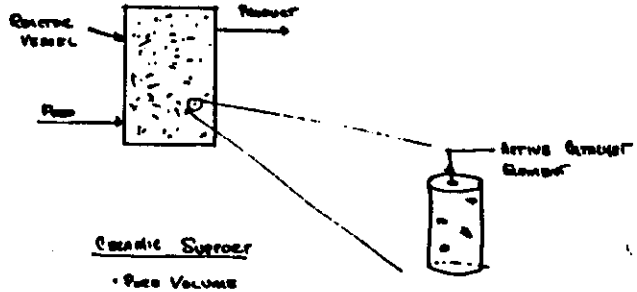
Chemical Conversions Are Accomplished By Several Means

+ Thermal Treatments

+ Catalysis (Homogeneous or Heterogeneous)
  - Minerals (Clays, Zeolites, ...)
  - Metals (Transition Metals, Noble Metals, Alloys)
  - Others (Silicon, Oxides)

(See, e.g. Satterfield, Heterogeneous Catalysis in Practice, McGraw-Hill, 1980)

Heterogeneous Catalysis: A Schematic



Ceramic Support

- Pore Volume
- Pore Size Distribution
- Macroscopic Dimensions
- Mechanical Properties

Hydrotreating Catalysis: A Specific Example

Goal: To upgrade crude oils and residua (8.9~950°C)

	Kuwait	Iranian Heavy	Arabian Heavy
Sulfur (wt.%)	4.21	2.72	4.31
Vanadium (ppm)	58	145	98
Nickel (ppm)	12.7	55.6	26.9
C_7 Asphaltenes (wt%)	2.7	8.6	6.5
Conrd. Carbon (wt.%)	9.8	10.0	13.1

Goals:
- Demetallization
- Heteroatom Removal (S + N)
- Molecular Weight Reduction

(See, *Catalyst Deactivation* 6 (Elsevier, 1980) p.55)

The Operating Catalyst is Quite Complex

Ex:

$$CoO + MoO_3 + \gamma\text{-}Al_2O_3 \xrightarrow[\text{Carbon}]{\text{400°C},\ ?\ S_x} \ ?$$

- Molybdenum Oxides / Sulfides
- Cobalt "Promoter" (Relationship to Mo ?)
- Alumina Support Effects
- Deposited Carbon
- Deposited Metals (V, Ni, ...)

⇒ Can One Define Catalysis ?
- + Molecular Mechanisms ?
- + Active Sites ?

MoS_2 is one of a Large Class of Layered Sulfides

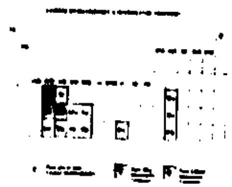
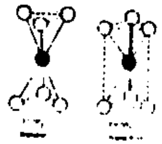


Fig. 1 The occurrence of layered dichalcogenides

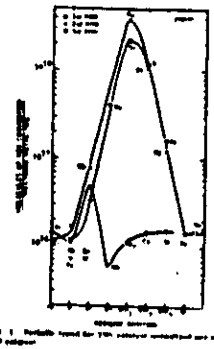


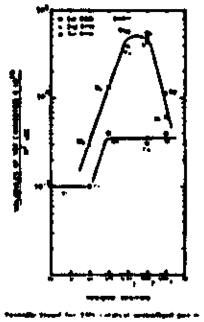
- + Superconductors, Semiconductors, Metals
- + Non-Stoichiometry
- + Intercalation

(See, Silbernagel, Mat. Sci. & Eng. 31, 281 (1977))

Model Reactions Probe Catalysis

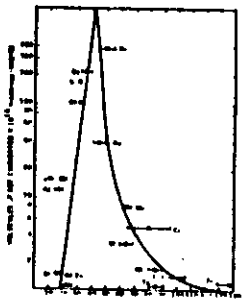
Example: Dibenzothiophene Desulfurization

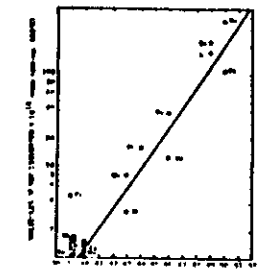




Trends: Electronic, Geometric, Chemical (Chianelli, Cat. Rev. Sci. Eng. 26, 361 (1984))

Relation To Bulk Physical Properties





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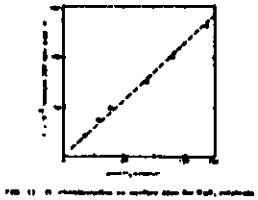
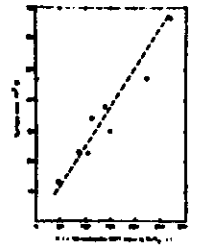
Oxygen Chemisorption, Surface Area of MoS_2 Track HDS Activity

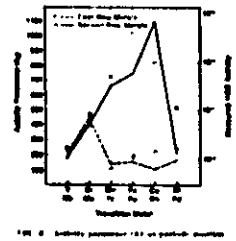




- Excellent Quality
- MoS_2 has a Hydro Treating - Not Lowered

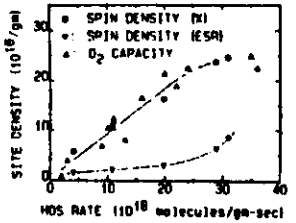
(illegible)

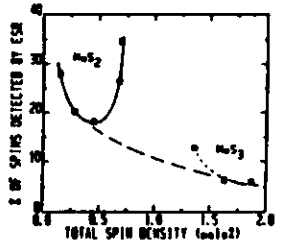
Activity Systematics Track Electronic Band Properties

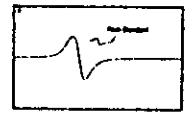


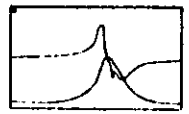
(illegible)

Magnetic Susceptibility, O_2 Chemisorption and ESR for MoS_2









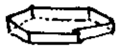
(illegible)

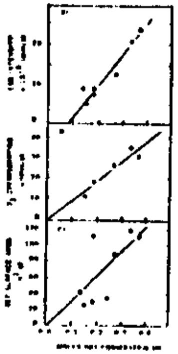
Surface Area Does Not Track HDS Activity for MoS_2

HDS Activity Does Track

- O_2 Chemisorption and
- Mo^{3+} Defect Density from Electron Spin Resonance

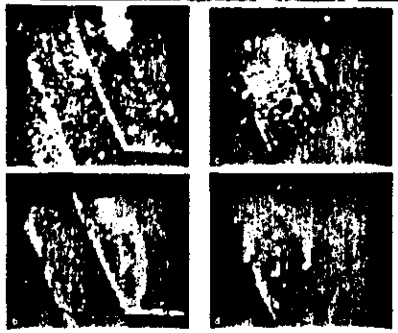
Suggests Edge Sites Are Active

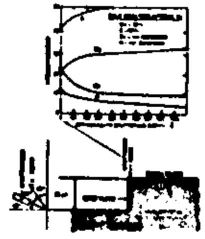


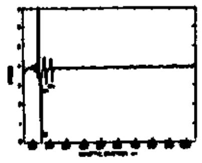


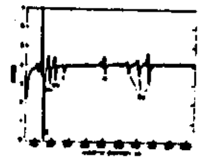
(Silbernagel, Pecoraro, Chianelli, J. Catalysis [illegible], ( ))

Auger Spectroscopy Establishes Edge Location of the Cobalt Promoter Atoms



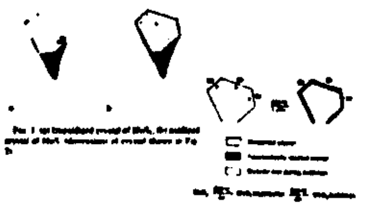






(Chianelli, et al., J. Cat. [illegible], [illegible] ([illegible]))

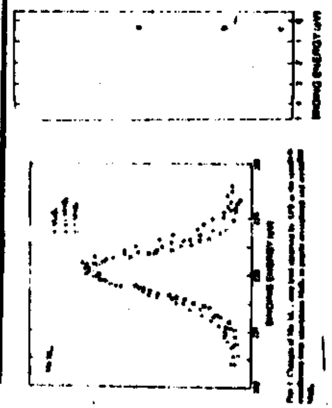
Electron Microscopy of MoS_2 Crystallites

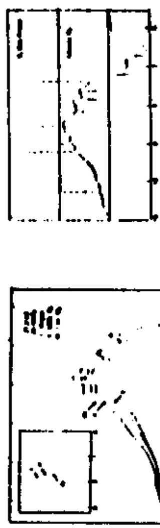


- Topotactic Reactions Are Common in These Oxide-Sulfide Systems

(Chianelli, et al., J. Cat. [illegible], [illegible] ([illegible]))

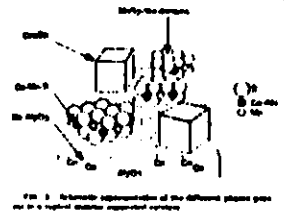
XPS, UPS Show Band Tailing in Amorphous MoS_2

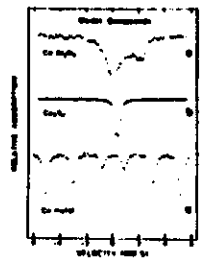


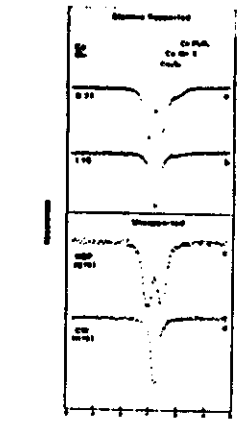


(Liang, Hughes, Chianelli, J. Vac. Sci. Tech. A2, [illegible] ([illegible]))

Mössbauer Spectroscopy Discriminates Cobalt Sites on Catalysts

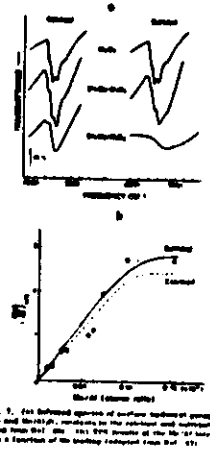


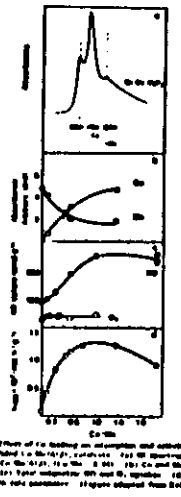




(Topsøe & Clausen, Cat. Rev. Sci. Eng. 26, 395 (1984))

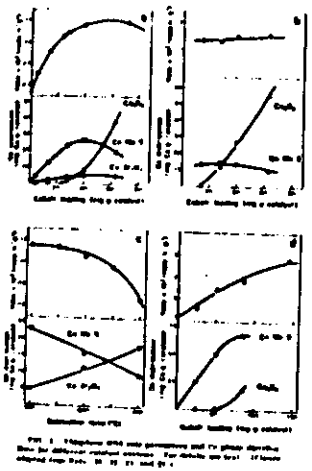
Adsorption and Surface Properties of $Co/Mo/Al_2O_3$ Catalysts

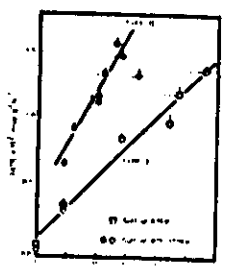




(Topsøe and Clausen)

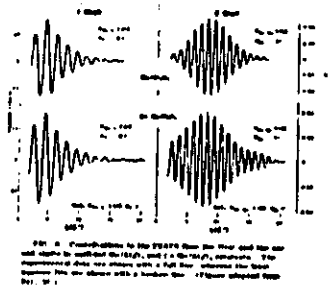
Catalytic Activity Tracks Amount of Co-Mo-S Phase



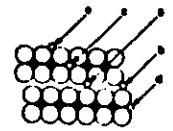


(Topsøe and Clausen)

EXAFS Measurements Support Small MoS_2 Crystallites on Catalysts



- ~ 10 Å
- Addition of Cobalt Promotes the Mo Edges
- Co appears to be on the crystallite Edges



(Topsøe and Clausen)

Coupling Chemistry and Characterization in the Work to Understanding Catalysis

- Molecular Conversion Probes
  - Reactants
  - Kinetics
- Catalyst Chemistry Variations
- Battery of Characterization Techniques
  - ESR
  - Mössbauer
  - EXAFS
  - UPS, XPS
  - NMR
  - Microscopy, Microprobe
  - Magnetic Susceptibility

  → In Situ
- Molecular Adsorption —
- Theoretical Solid Consistency