

Identifying Potential-Focus on Catalyst Application

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PERSPECTIVE IN ENERGY CONVERSION

- Utilize processes that have increased feed stock flexibility
- Explore new routes to increase energy efficiency
- Minimize/reduce environmental impact and/or provide downstream environmental solution
- Evaluate Processes on full cycle of **WELL TO WHEEL** including environmental cost

**CATALYTIC PROCESS TECHNOLOGIES VITAL IN
CREATION OF ENERGY CONVERSION NETWORKS**

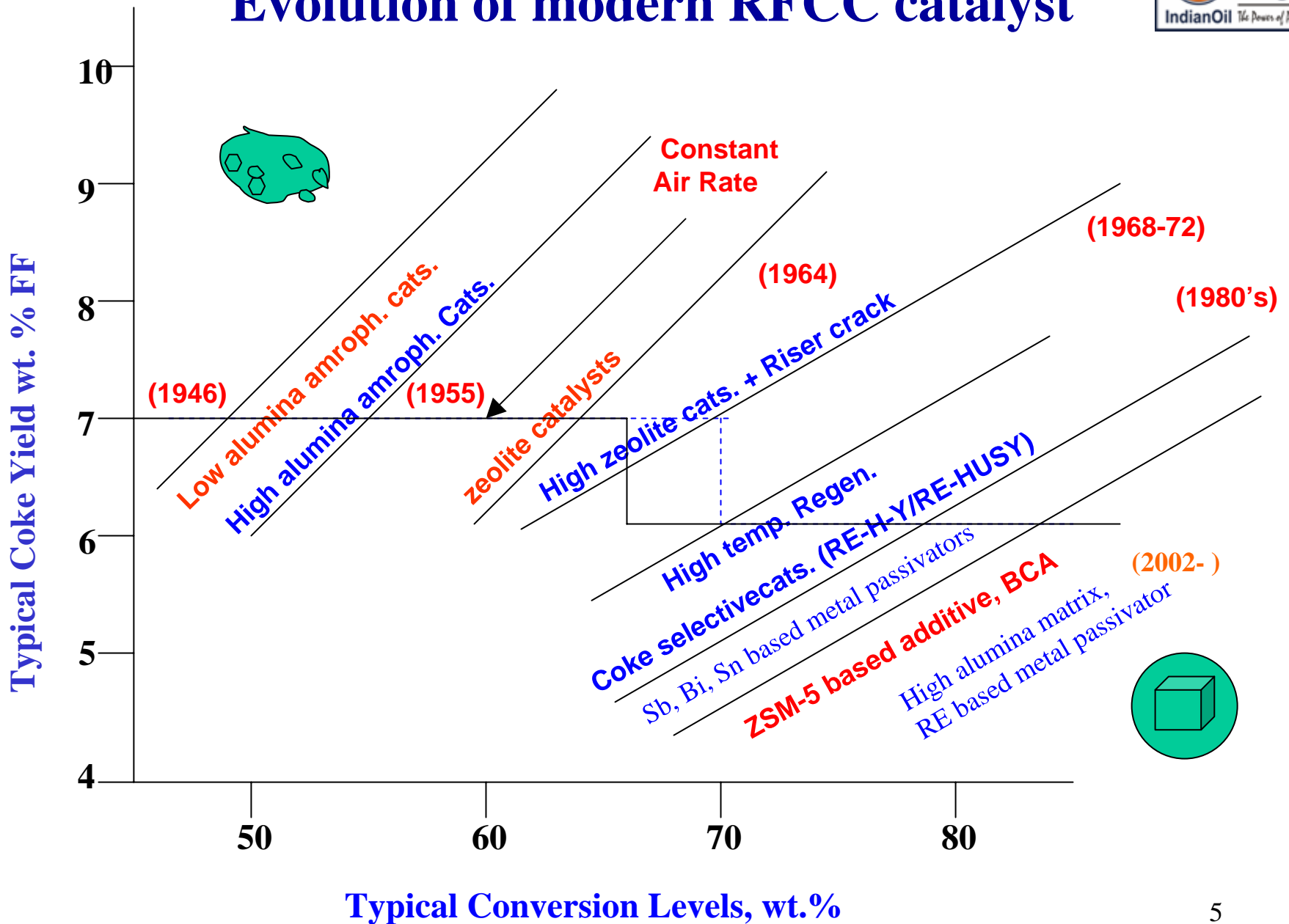
REFINING: SUSTAINABILITY OF OPERATION

- **Crude sourcing**
 - **Cost at refinery gate**
 - **Quality of crude**
- **Economy of scale of operation**
 - **Size of operation**
 - **Choice of technology**
- **Integration of plant for value addition**
 - **Minimize energy consumption**
 - **Value added product portfolio**
- **Environmentally sustainable operation**

INNOVATION IN CATALYSIS: SOLUTIONS FOR MODERN PETROLEUM REFINING

- **Catalysts to Meet Increased Demand for Cleaner Fuels**
- **Catalysts for selective chemical transformations for value added chemicals**
- **Requirement for High Activity Catalyst with Increased Life Cycle to Offset Diminishing Refinery Margins**

Evolution of modern RFCC catalyst



SCIENTIFIC INNOVATIONS IN FCC CATALYST DEVELOPMENT

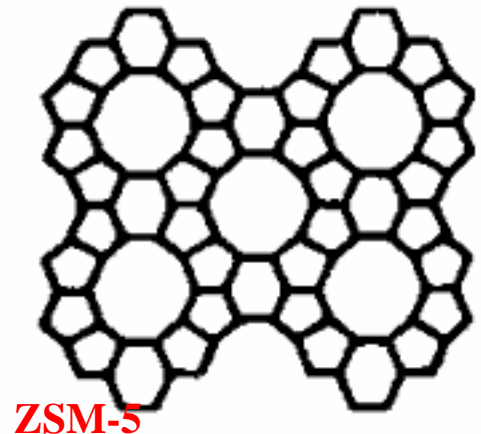
- **More active binding materials/ matrix**
- **Improved catalyst assembly technology and control of pore architecture**
- **Better understanding of reaction kinetics**
- **Improved regeneration kinetics and control over regeneration**
- **Improved Zeolite accessibility**
- **Improvement in catalyst activity testing methodology**

Low coke make cracking components

- ZSM-5 zeolite (~ 5.4 Å pore dia.)
- USY (~ 6.4 & 13 Å pore dia.)
- Alumina

Low coke make processes

- IndMAX over Conventional pure Y zeolite FCC
- Indalin and Indalin Plus over FCC



Reduction in catalytic coke is key to enhance valuable products

Catalyst systems for lower coke generation

Component	Yield wt% FCC Catalyst W/F = 3.5	Yield wt% IndMAX Catalyst W/F = 3.5
LPG	25	35
Gasoline	30	21
TCO	22	21
Bottom	4.5	4.5
Coke	11.0	9.0
Conversion	82	81

Efficient coke combustion and heat utilization

- **Application of CO-Combustion promoter in RFCC**
- **Reduction in CO emission**
- **Enhanced catalyst temperature and improved conversion**

Enhanced FCC efficiency with CO promoter additive

Parameter	Base Case	With CO Promoter
Yield, wt%		
Dry Gas	2.60	2.60
LPG	11.20	11.20
Gasoline	23.50	26.50
TCO	41.70	42.00
CLO	16.00	13.00
Coke	5.00	4.50
Feed, T/D	3770	3850
Dense Temp.	630	648

- **Monometallic Catalysts**

Platinum (<0.5 wt%) dispersed uniformly over high purity chlorinated alumina support

- **Bi-metallic Catalysts**

- **Better activity**
- **Improved selectivity**
- **Increased stability**
- **Resistance to deactivation due to coke**
 - **5-12 % monometallic catalysts**
 - **10-40 % bimetallic catalysts**

Metal platinum = 0.2 - 0.6 wt%

Metal promoters = Ir, Re, Ge & Sn (0.03 - 0.7 wt%)

Chlorine contents = 1.0 - 1.2 wt%

MULTIMETALLIC CATALYST ARE ALREADY AVAILABLE COMMERCIALY

SCIENTIFIC INNOVATIONS IN HYDROPROCESSING CATALYST DEVELOPMENT

- Introduction of new Zeolite families for application in hydrocracking, hydro-dewaxing etc
- Improved methodologies for obtaining better metal dispersions
- Increased understanding of the working of catalyst active sites, like knowledge of high active Type II sites.
- Improved carrier design, like the control on pore size distribution, pore architecture
- Increased understanding on the reaction kinetic and its exploitation
- Improved fixed bed catalyst loading

SOLUTIONS FOR MEETING ENVIRONMENTAL REGULATIONS FOR DIESEL

SULFUR CONTENT : Diesel hydrodesulfurisation

- **Better knowledge about the hydrodesulfurisation kinetics of different components**
- **Increase in catalyst activity**
- **Improvement in reactor internals**
- **New concepts in reactor design**

SOLUTIONS FOR MEETING ENVIRONMENTAL REGULATIONS FOR DIESEL

CETANE NUMBER: Diesel Hydrotreatment

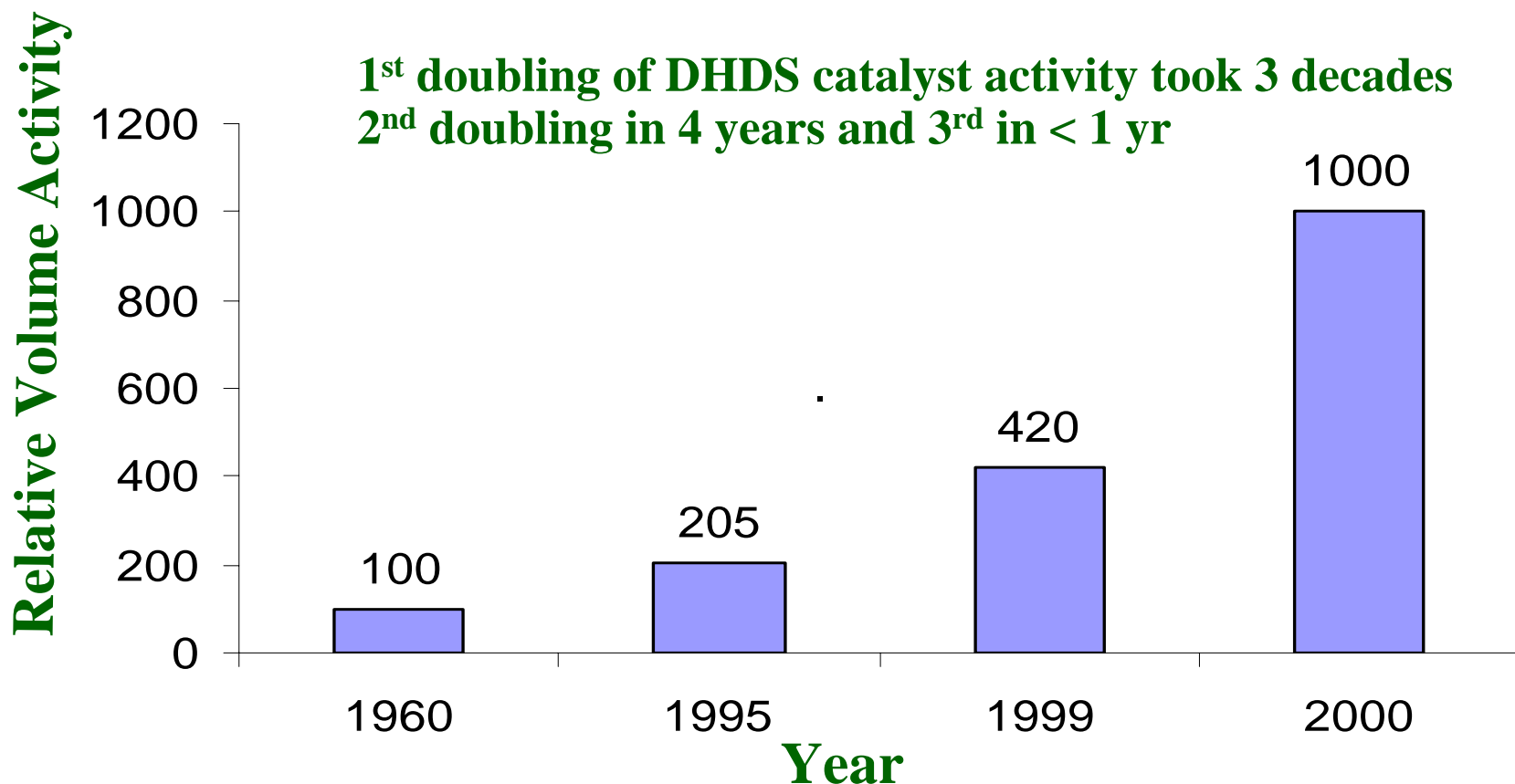
- **Cetane number improves with aromatic saturation**
- **Cetane number of FCC LCO and CGO streams can not be increased beyond 45 by saturation alone**
- **In addition to saturation of aromatic rings, ring opening is also required**

SOLUTIONS FOR MEETING ENVIRONMENTAL REGULATIONS FOR DIESEL

T95 POINT REDUCTION: Distillation, Diesel Hydrotreatment, Mild hydrocracking

- No standard technology exists for lowering T95 point
- Distillation option would lead to loss of diesel yield
- Aromatic saturation and hydro-isomerisation can reduce the end point by few degrees
- Selective ring opening and mild hydrocracking can shift T95, but at the expense of some yield loss

DEVELOPMENT IN DIESEL HYDROTREATING CATALYST TECHNOLOGY



Intensive efforts world over for development of high active DHDS catalyst

Naphtha conversion Technologies:

IOC R&D's novel process **Naphtha Hydrocracking to LPG**

- Naphtha Hydrocracking process (Fixed bed reactor) to LPG & Gasoline
- Catalyst jointly developed by IOC-R&D and M/s. Zeolyst International
- **Indalin + Technology**
 - Naphtha cracking process (FCC) to LPG & Gasoline
 - Proprietary tailor made catalyst formulation

Naphtha conversion Technologies: Naphtha Hydrocracking to LPG

- Flexible Process for Maximization of LPG (upto 80 wt%) or Gasoline (upto 75 wt%)
- Employs easy to operate Fixed Bed Reactor Technology –SSOT configuration
 - Low Hydrogen Partial Pressure : 15-80 bar
 - Catalyst Average Temperature : 300-410oC
 - Liquid Hourly Space Velocity : 0.5-4 hr-1
 - Hydrogen Consumption : 1.5-3.5 wt%

Naphtha conversion technologies: Indalin+ Technology

- **Converts all types of naphtha to high yield of saturated LPG and high octane gasoline with low olefins content**
- **LPG : 45-55 wt% of feed - comprising saturates > 80 wt%**
- **No feed pretreatment**
- **No requirement of external hydrogen supply**
- **Proprietary tailor made catalyst formulation**
- **Flexibility of varying LPG/gasoline ratio as per seasonal product demand**
- **Can be integrated to aromatic complex for petrocheml feed (BTX)**
- **Relatively lower investment and operating cost**

VGO Hydrocracking to Maximum LPG / ATF Catalyst

Conventional Catalyst System

- Higher zeolitic hydrocracking catalysts leads to higher LPG along with high yields of low value fuel gas & naphtha
- Issue: Increase in LPG / ATF without concomitant increase in LN / Gas make

Customised Catalyst System (IOC-R&D and Zeolyst)

- ✓ Selective Zeolite Cracking Catalysts to Increase LPG without increasing Light and Heavy Naphtha make significantly

CONVENTIONAL RESIDUE HYDROPROCESSING: THE PROBLEM

Catalyst Deactivation

- Pore mouth plugging of catalyst particles
- Metals (V, Ni) poisoning of active sites
- Coke deposition

Interstitial Deposition

- Iron depositions in the bed
- Fouling
- Asphaltene flocculation

Approaches: Use of graded beds, moving bed, ebullated bed processes

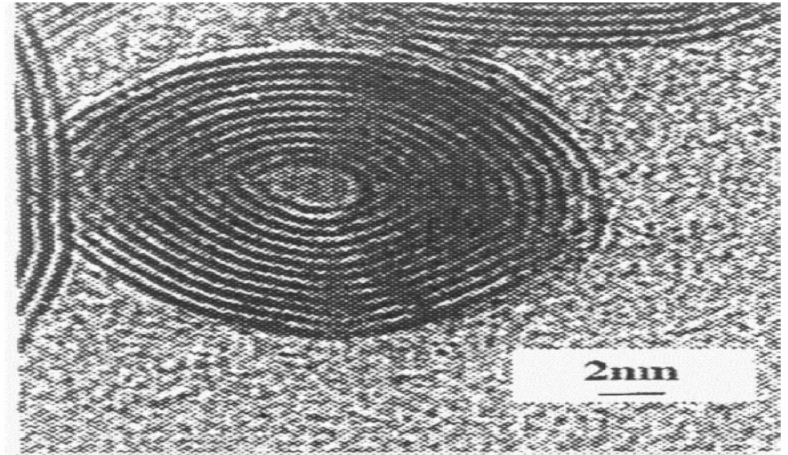
If resid molecules can't reach catalyst sites, why not catalyst reach them ! - **Nano sized in situ generated catalyst systems**

Some single layered MoS₂ structure

Single Layered Transition Metal Sulfides

➤ Catalyst Precursors

- Influences the type of SLTMS generated



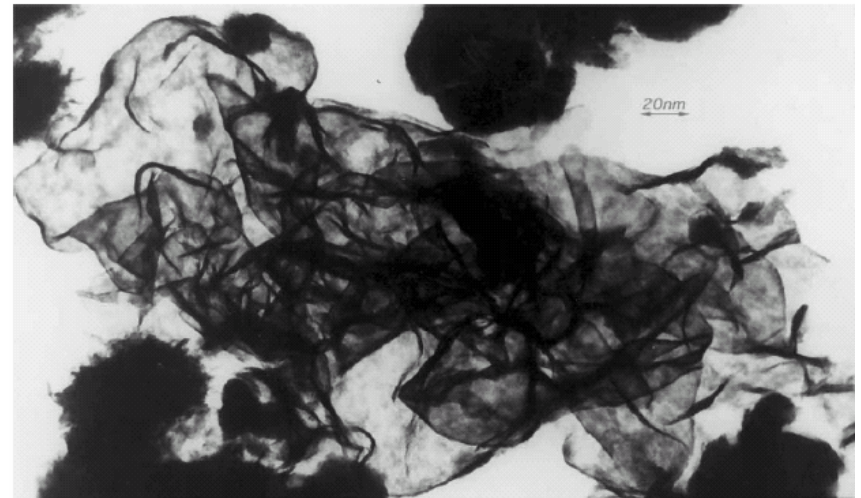
➤ Stabilized Catalysts

- Sulfidation: MoS_{2+x} (0 < x < 0.5)
- Catalytic conditions: MoS_{2-x}C_y (0 < y < 1)

MoS₂ Russian Doll structure

Values of x and y will increase with decrease in particle size

Catalytic properties of the system depends on the system generated



MoS₂ Rag structure

Process based on SLMTS	Catalyst	Ref/Licensors
Microcat RC	MoS ₂ /H ₃ PMo ₁₀ O ₃₄ (100-300 ppm)	Exxon Mobil US Patent 4134825
Eni-Est	OIL SOLUBLE METAL SALT (Ni, FE)	NPRA 2003
Super Oil Cracking	MoS ₂ + C black (<1.0 wt%)	Chiyoda Japan
High Conversion Hydrocracking Homogenous Catalyst	MoS ₂ /Mo-ethyl hexanoate < 150 ppm MoS ₂	Alberta Energy
Activated Slurry Hydrocracking	MoS ₂	Chevron
Aurabon	VSx/VOSO ₄ (2-6 wt%)	UOP
Combi Cracking	Coal char, iron ore, red mud, 1-3 wt%	Veba Oil
Can Met	Fe ₇ S ₈ /FeSO ₄ , coal (1-2 wt%)	Petro Canada
Hydrocracking Distillation Hydrotreating	Ore of Iron Laterite (1-3 wt%)	US Pat

Conclusion

- **Catalysts are integral to refinery sustainability and profitability, owing to the challenges**
- **Research driven Innovations towards development of tailor-made catalysts is the key to success**
- **Case studies and applications from Indian Oil show the efficacy of the approach**