



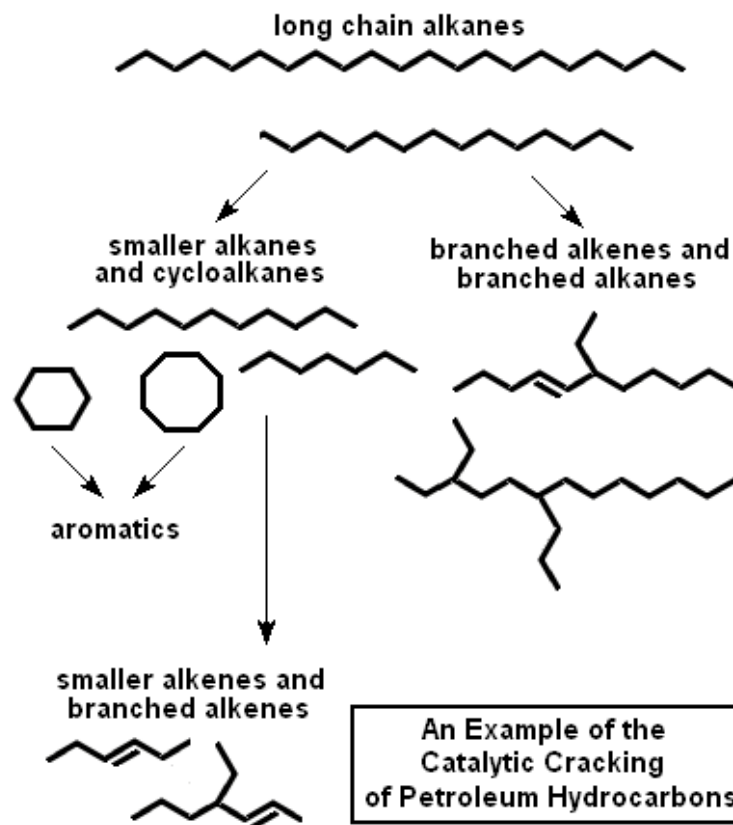
## CATALYSIS AND DESIGN PROJECT REPORT

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- Catalytic cracking involves the conversion of large molecules and heavy organics into low molecular fractions, aromatics, and olefins.
- These heavy molecules are formed by fragmentation and re-polymerization during pyrolysis.



## ■ INTRODUCTION

- Catalytic cracking process of hydrocarbons utilizing crystalline aluminosilicates
- Decrement of olefin and increment of octane number for productions of clean fuels
- Effective approach for the need of high-quality gasoline is to develop the novel zeolite materials added to FCC catalysts
- The type of zeolite L with the hexagonal crystal system, wide pore size, unique adsorptive and catalytic properties have been employed

## ■ CATALYTIC TESTS

- Catalytic cracking tests were performed at a MAT (micro activity test) unit with a RE-USY base catalyst and two blends respectively
- Light diesel oil was used as a feedstock in the catalytic cracking tests
- The cracking products were analyzed using a gas chromatograph equipped with a FID detector using a capillary column





- HISTORICAL TRENDS

- Catalytic cracking is at present a major process to produce gasoline
- The technology of catalytic cracking has seen many innovations and developments
- Developments in the cracking catalyst
- Amorphous silica-alumina catalysts with relatively low alumina content
- Zeolites as partial replacement for amorphous silica-alumina in the mid sixties
- Success of zeolites in FCC is mainly based on their higher intrinsic activity
- Better selectivity towards gasoline as compared with amorphous catalysts, and their good activity retention
- Riser cracking, in which contact times are of the order of seconds



- CATALYST DEACTIVATION
  - All reactions of organic compounds on solid catalysts are accompanied by the formation of heavy by-products, the so-called coke
  - Coke is formed inside the pores and/or the external surface of solid catalysts and is the primary cause of their deactivation.
  - Product composition, coke rate and coke composition are dependent on various parameters, such as reaction temperature, nature of the reactants, and the physicochemical characteristics of the zeolites, such as acidity and pore structure
  
- REACTION KINETICS AND CATALYTIC PROCESSES
  - On studying the catalytic cracking of methylcyclohexane over an industrial FCC catalyst High selectivity towards toluene were observed ( $S_{tol} \approx 70\%$ ).
  - The unusual product distribution originates from a predominant protolytic cracking that is favored by the low pressures and high concentration of acid sites applied in the TAP reactor
  - The formation of the other cracking products (benzene and smaller paraffins and olefins) is well accounted for by the relative stability of the secondary and tertiary carbenium ions.





## ■ EXPERIMENTAL

- The catalyst was diluted with inert particles in order to diminish the cooling of the bed due to the vaporization and the endothermic cracking reactions.
- The residence times of the pulses were varied by changing the flow rates of the carrier gas (helium) and the catalyst-to-oil ratio was varied by changing the amount of the catalyst in the inert material
- During catalyst regeneration process the product stream containing CO and CO<sub>2</sub> was split into two streams
- Experimental conditions: Temperature - 500 and 700 °C catalyst-to-oil ratios - 1 and 44 g<sub>cat</sub>/g<sub>oil</sub> residence times - 16 and 200 ms.

## ■ PROCESS ANALYSIS

- Fluid bed technology is important in the oil, petrochemical, pharmaceutical, and food industries
- In a fluidized bed, an upward current of gas suspends particles. The particles move upwards in the center of the bed and fall downwards, under gravity, at the walls
- In dense beds a 'bubble phase' is often seen. The bubbles are responsible for much of the mass transport of particles and are an important part of the mixing process.
- Fluid beds produce large levels of acoustic emission.
- Anything in the fluid bed, which changes the velocity, size, or hardness, brings about a change in the acoustic emission signals detected.





- The feedstock to the FCC unit is preheated to about 260 °C (500 °F) and then brought to reaction temperature when mixed with powdered catalyst
- The feed is cracked and vaporized while traveling up the riser and then separated quickly to prevent over cracking and a loss in gasoline production
- The cracked product is sent to cyclone vessel to remove catalyst and then sent to a distillation column for separation into fractions.
- The deactivated catalyst is then fed to the regenerator where it is fed with combustion air to burn off the coke.
- FCC catalysts are nowadays based on zeolitic materials together with binders and promoters of various sorts.
- Essential for the operation of a good cracking catalyst is the presence on the surface of the catalyst of strong acidic sites that can initiate the reaction by forming carbonium ions that then react further to form carbonium ions
- The carbonium ions can then react yet further in many ways including by hydrogen transfer
- C–C bond scission and isomerization
- When a hydrocarbon encounters a metal or oxide surface on which a reaction will occur, it first becomes adsorbed on that surface. Then, if the temperature is sufficiently high, it will undergo further interaction, producing new surface species that can then desorb to give products.





## ■ INTRODUCTION

- Hydrogen is an industrially important material and is mainly produced from hydrocarbons out of which methane has a highest H/C ratio and methane cracking also hydrogen with impurity mainly of unreacted methane
- Nickel is widely used as a catalyst for methane cracking but is has a problem of rapid deactivation.
- In methane cracking, the catalyst support plays an important role. A desirable support is one which does not significantly interact with the metal particles, provides good catalyst distribution, and minimizes

## ■ EXPERIMENTAL METHODS

- The catalyst was prepared by wet impregnation of alumina using an aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- The nickel amounts were checked using a Prodigy/Prism high dispersion ICP
- Methane cracking was studied through thermogravimetry analysis
- Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study catalyst morphology
- Nickel dispersion was measured using hydrogen chemisorption on a Hiden Catlab Microreactor

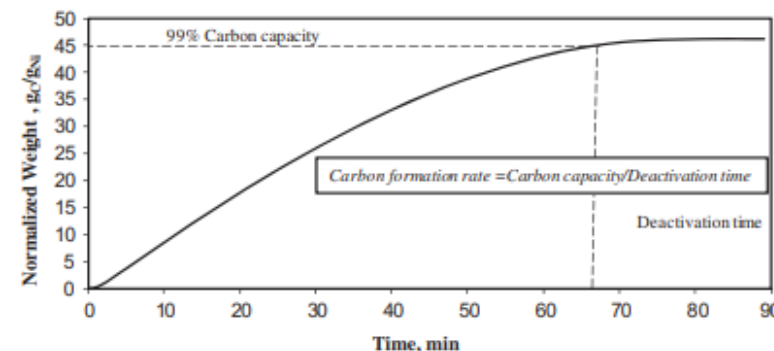






## ■ EFFECT OF GAS FLOW RATE

- At 500 and 550 °C, increasing the flow rate has little effect on carbon capacity.
- At higher temperatures (600 and 650 °C) similar changes in flow rates lead to a decrease in carbon capacity.



**Fig. 1 – Normalized weight change for the porous catalyst in g<sub>C</sub>/g<sub>NI</sub> at 550 °C, 120 ml/min, 100% methane, and 1 atm.**

## ■ EFFECT OF HYDROGEN PARTIAL PRESSURE

- Increasing hydrogen in the inlet gas leads to a decrease in the reaction rate, and the time required for deactivation increases due to the slower rates.
- However, increasing the hydrogen partial pressure to 0.15 atm resulted in a rapid drop in carbon deposition rate and an associated increase in deactivation time
- An additional increase in hydrogen partial pressure to 0.2 atm resulted in almost no carbon deposition





## EFFECT OF METHANE PARTIAL PRESSURE

- The effect of methane partial pressure was studied by varying the methane content from 50 to 100%, balanced with nitrogen at atmospheric pressure

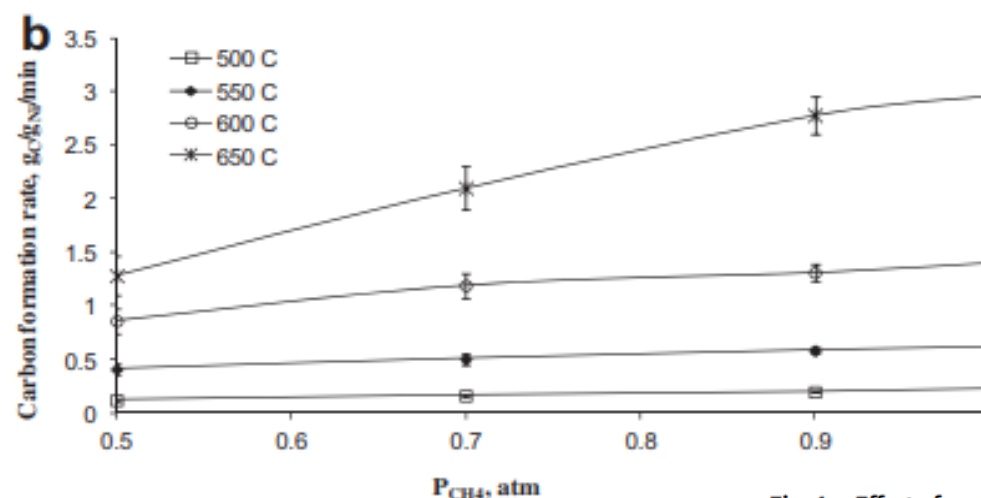
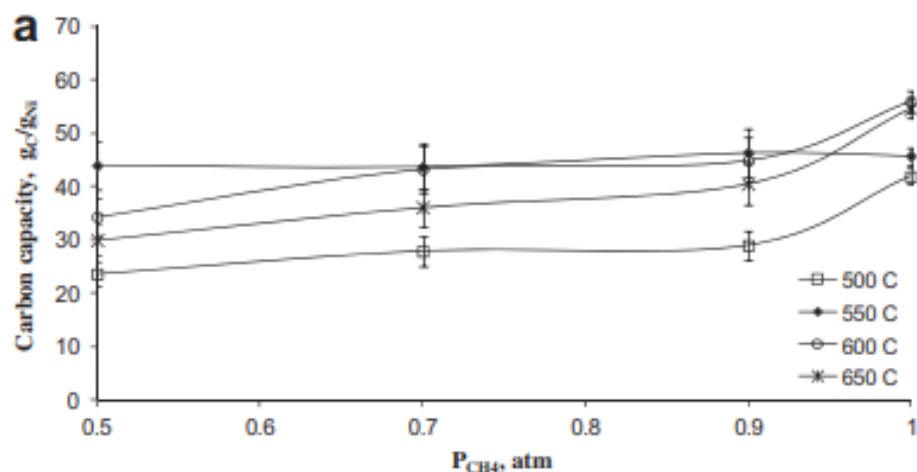


Fig. 4 – Effect of methane partial pressure on a) carbon capacity and b) carbon formation rate. Conditions: 725  $\mu$ m porous catalyst particle diameter, 120 ml/min, balance nitrogen.

## EFFECT OF TEMPERATURE

- At the highest flow rate (240 ml/min), the carbon capacity is higher at **550 C** than at all other temperatures





- The catalyst deactivates during the cracking reaction due to carbon build-up. Periodic regeneration is therefore necessary
- The rate of regeneration of the non-porous catalyst was faster than that of the porous catalyst at both 500 and 550 C.
- Six cycles were enough for the non-porous catalyst to lose its activity, while the porous catalyst remained active even after 24 cycles.
- For the non-porous catalyst, the XRD results show that a new phase,  $\text{NiAl}_2\text{O}_4$ , appeared after regeneration. The formation of  $\text{NiAl}_2\text{O}_4$  reduced the total surface area of active nickel available for the reaction leading to the rapid decrease in cracking performance
- The two main reasons for rapid deactivation of the non-porous catalyst over a few cycles are 1) formation of inactive  $\text{NiAl}_2\text{O}_4$  and 2) Ni sintering
- The carbon deposited on the non-porous catalyst formed carbon agglomerates while the carbon deposited on the porous catalyst formed hollow carbon filaments
- The carbon deposited during the cracking/regeneration cycles experiments was oxidized using air at 550 C in the TGA. These three stages( I II III) indicate the presence of different types of carbon : Ca, Cb, and Cg. Ca is the easiest to gasify, whereas Cg is the hardest to gasify.(a,b,c are to be read as alpha ,beta and gamma)



## ■ INTRODUCTION

- Main process for producing hydrogen is steam reforming of natural gas
- Result of methane cracking, only hydrogen is produced as a gaseous product in a mixture with unreacted methane
- Early methane cracking was done in fire-brick furnaces at 1500 °C to produce soot
- major challenge in a continuous process for hydrogen production using methane catalytic cracking is the regeneration of the spent catalyst

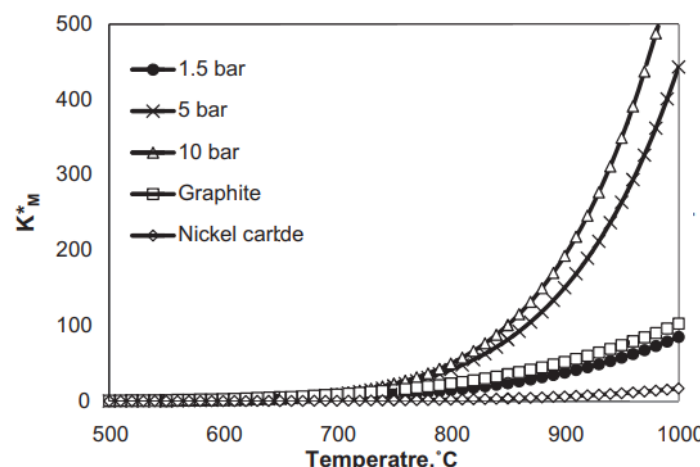


## ■ THERMODYNAMICS OF METHANE CRACKING

- equilibrium constant expressed in terms of the partial pressures of CH<sub>4</sub> and H<sub>2</sub>
- equilibrium constant can be predicted from Gibbs free energy equations and temperature dependent equations

$$K_P = \frac{(p_{\text{H}_2}^2)_{\text{eq}}}{(p_{\text{CH}_4})_{\text{eq}}}$$

$$K_{\text{CH}_4/\text{H}_2}^{\text{sol}} = \frac{(p_{\text{H}_2}^2)_{\text{eq}} c_{\text{CH}_4/\text{H}_2}^{\text{sol}}}{(p_{\text{CH}_4})_{\text{eq}}}$$



**$K_M^*$  versus temperature at different methane partial pressures**

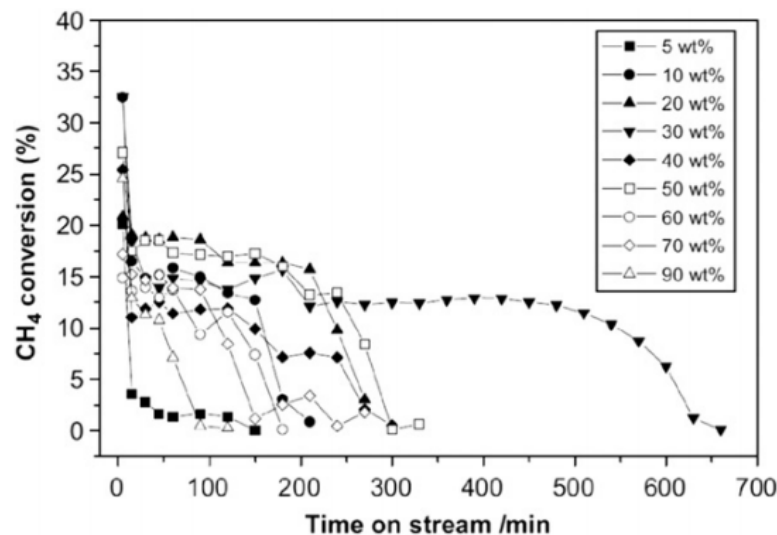


## ACTIVE PHASE

- The catalyst function is to reduce the activation energy required for methane decomposition
- Iron group metals are known to have the highest activity for hydrocarbon cracking  $\text{Ni} > \text{Co} > \text{Fe}$
- Temperature, electronic state and dispersion, affect nickel's stability and activity for methane cracking

## SUPPORT MATERIAL

- The support material also directly affects methane conversion by affecting the surface area of metal subjected to the reaction and the metal's electronic state
- The support structure and textural properties (e.g. porosity) also affect methane conversion
- support structure may also affect the outlet gas composition and the morphology of the deposited carbon

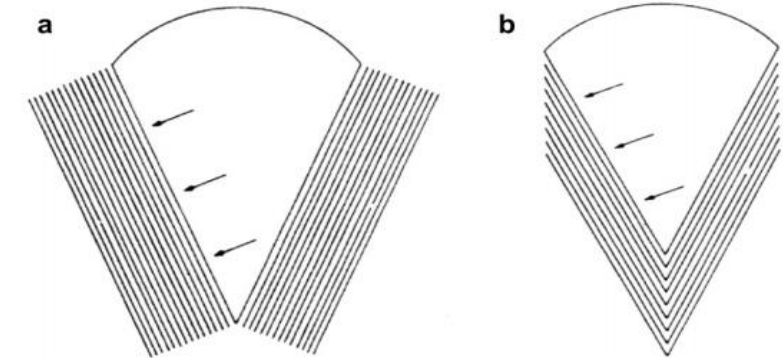
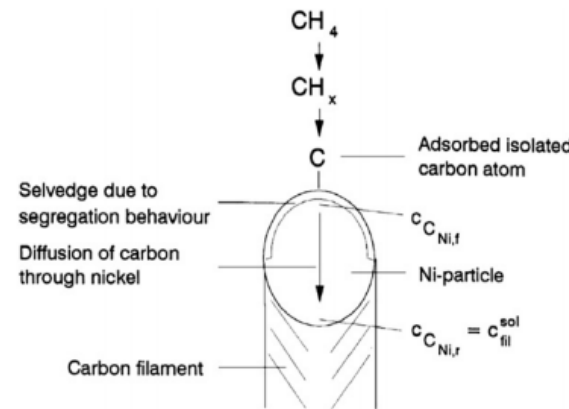


**Methane conversion over various Ni/SiO<sub>2</sub> catalysts**



## OVERVIEW

- Types of coke that form during methane cracking on supported metal catalysts, namely polymeric, filamentous, and graphitic carbon.
- Multistage process that starts with methane adsorption followed by several dehydrogenation reactions and ends with coke formation



**Cross sections of conical graphite layers excreted**

## NUCLEATION

- First stage in which nickel possesses liquid properties
- Nucleation is due to 1) high carbon coverage on the Ni surface, 2) subsequent high concentration of carbon dissolved in the nickel particle and 3) carbon segregation behavior



- FILAMENT GROWTH
  - Ni particle detaches from the support surface
  - Concentration of the carbon at the metal/filament interface drops to the saturation concentration
  - A uniform temperature on the nickel particle prevails due to the balance between the heat losses and the heat gains from the surrounding environment, and the number of filaments remains constant
  
- DEACTIVATION OR TRAILING STAGE
  - Due to the presence of excess carbon on the gas side of the nickel surface, some carbon deposits on the nickel surface
  - A gradual decrease in available nickel surface area for methane cracking occurs
  - Less heat input to the metal particle, which decreases the rate of carbon diffusion through the nickel particles
  - Active nickel particles ultimately become completely encapsulated by carbon and filament growth ceases





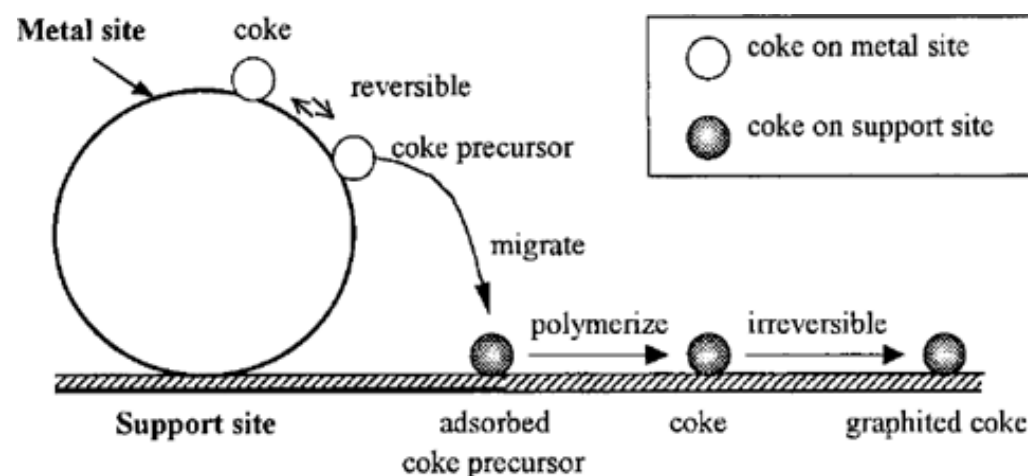


## ■ COKING

- The main deactivation mechanism during methane catalytic cracking is coking
- Defined as the physical deposition of carbonaceous species from the reacting species onto the catalytic surface
- May result in loss of catalytic activity as a result of blocking of catalyst sites and/ or pores

## ■ COKING DEACTIVATION MECHANISM

- Carbon is deposited on the active site at the active site/gas interface forming a layer called encapsulating carbon, which blocks reactant access

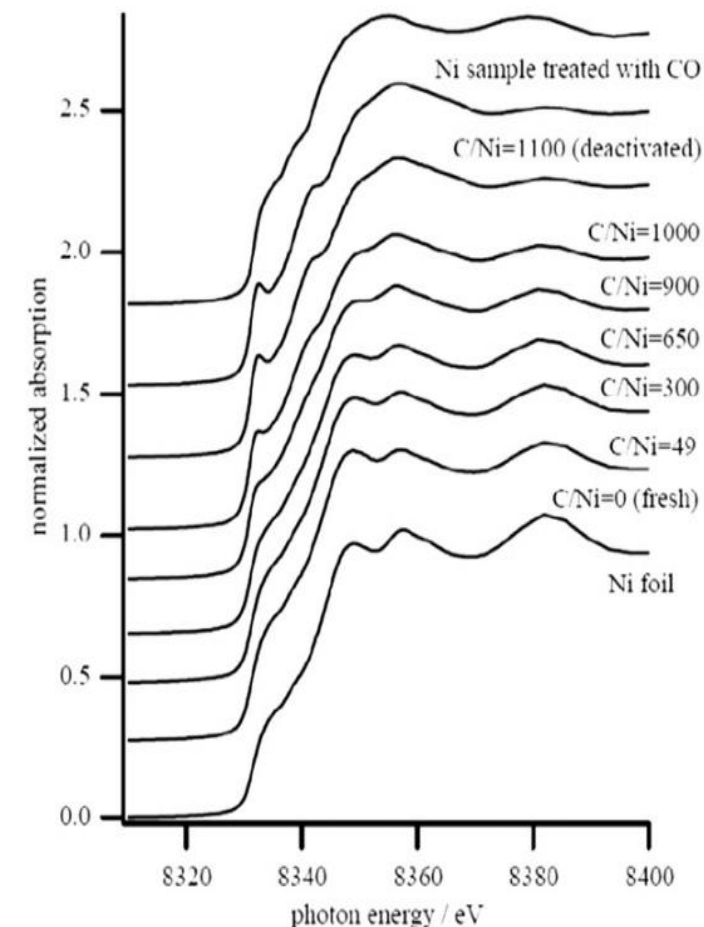
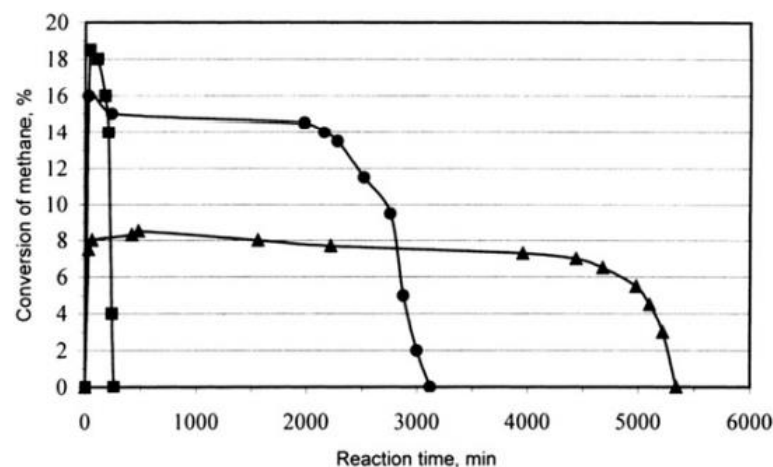
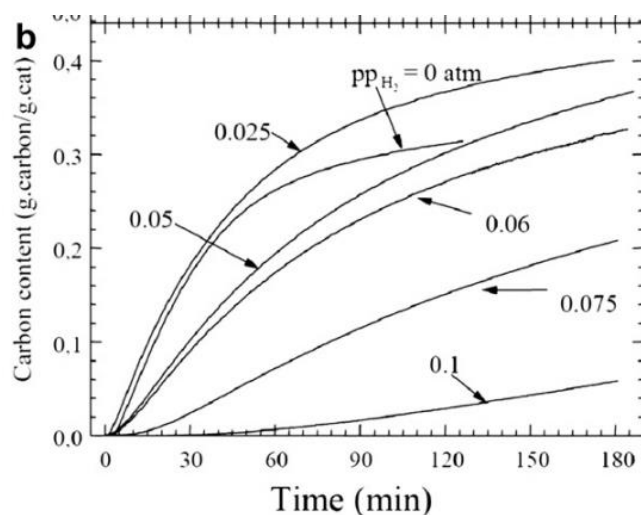






## FACTORS AFFECTING CATALYST DEACTIVATION

- The operating conditions have most effect on deactivation rate
- Methane flow rate (or more specifically the gas hourly space velocity, GHSV),
- Reaction temperature, methane partial pressure & hydrogen partial pressure
- The higher the temperature and methane flow rate, the shorter the catalyst life
- Increasing the flow rate or the reaction temperature decreased catalyst lifetime
- Increasing PCH<sub>4</sub> increased cracking and deactivation rates
- Hydrogen reduces both the cracking rate and the deactivation rate



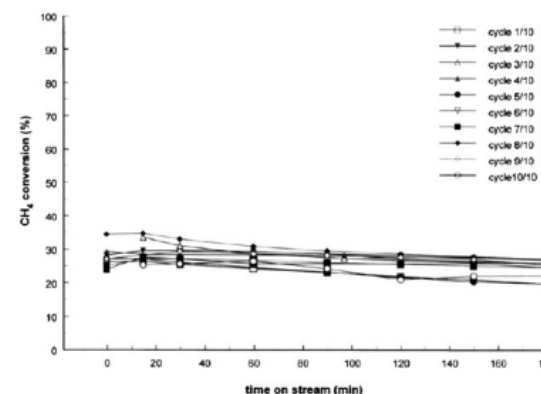


## AIR REGENERATION

- The catalyst was quickly and fully regenerated using air oxidation
- the high temperature generated during the oxidation process resulted in disintegration of the sample to a fine powder

## STEAM REGENERATION

- Two stages, first stage only pure hydrogen is produced, while in the second stage hydrogen contaminated with carbon monoxide and carbon dioxide is produced



## CO<sub>2</sub> REGENERATION

- The high temperature required to effectively eliminate all the residual carbon affected the textural parameters of the catalyst



- DETAILED MECHANISM RATE EQUATIONS
  - Models assuming non-dissociative adsorption of methane
  - Models assuming dissociative adsorption of methane
- MATHEMATICALLY FIT RATE EQUATIONS
  - Cato'n et al. Model
  - Villacampa et al. Model
- GLOBAL RATE EQUATIONS MODEL
  - Fukada et al. rate equation

$$k_{\text{decomp}} = 3.09 * 10 \exp(-29.5 \text{ [kJ/mol]}/R_g T) \text{ s}^{-1}$$

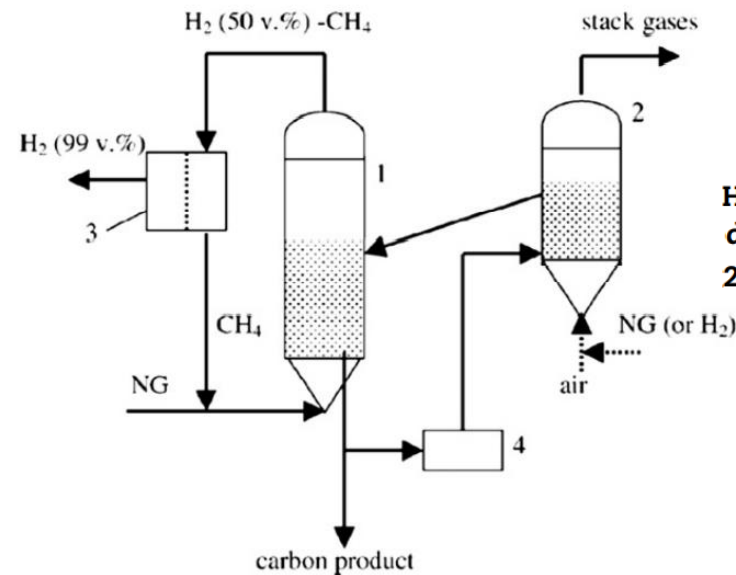
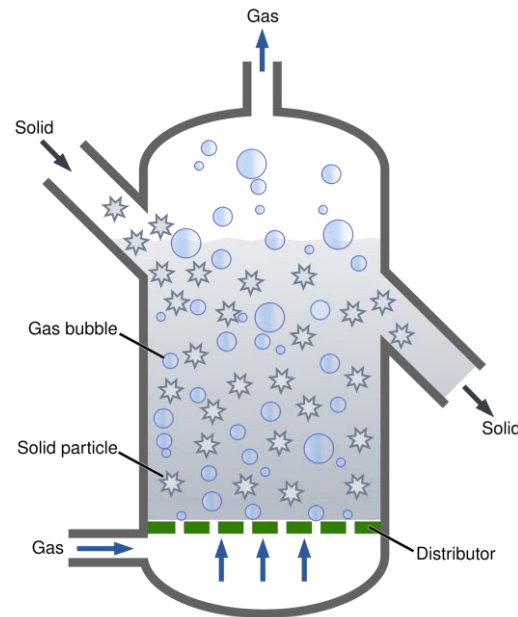
- Muradov et al. rate equation

$$-r_{\text{CH}_4} = k * P_{\text{CH}_4}^{0.5}$$



## ■ PROCESS ECONOMICS

- Advantages are ease of temperature control, ease of maintaining a constant temperature in the bed due to vigorous mixing provided by fluidization, enhanced heat and mass transfer, and low cost of catalyst handling.
- While the ratio of hydrogen produced per mole of methane fed is lower in methane catalytic cracking due to the absence of steam, fluidized bed catalytic cracking unit has cost advantages over steam reforming units
- The fluidized bed catalytic cracking unit should contain two fluidized bed reactors; one for cracking and one for regenerating the catalyst



**Hydrogen production by the thermo catalytic decomposition of natural gas: 1—fluidized bed reactor, 2—heater, 3—gas separation unit, 4—grinder**



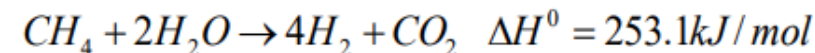
- REACTION TEMPRATURE
  - Increasing the reaction temperature increases the initial reaction rate
  - Deactivation becomes faster at higher reaction temperatures due to rapid carbon deposition, which blocks the active sites
  
- GAS VELOCITY
  - Fluidization quality or the gas solid contacting pattern is strongly dependent on gas velocity
  - If the gas flow rate is higher than that corresponding to the minimum fluidizing velocity, bubbles can form, which reduces the contact between the gases and catalyst
  - A lower gas velocity reduces the throughput of the reactor and will not induce fluidization
  
- PARTICLE SIZE
  - Geldart A (30e100 mm) type particles are used
  - These type particles lead to smooth fluidization, give better contact between the gas and catalyst, and achieve higher catalyst effectiveness factors
  - Smaller the particle size, the higher the methane conversion due to the higher surface area





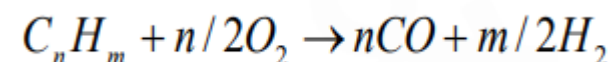
## ■ STEAM REFORMING

- Multi state process , most important and widely used
- Natural gas (NG) is the main reactant
- React with steam (H<sub>2</sub>O) and through a dehydrogenation process free hydrogen is produced



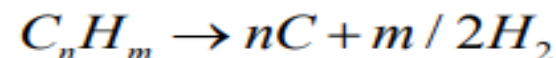
## ■ PARTIAL OXIDATION

- Best renewable ways of hydrogen production
- Final product of partial oxidation is CO and H<sub>2</sub>
- Highly exothermic reaction



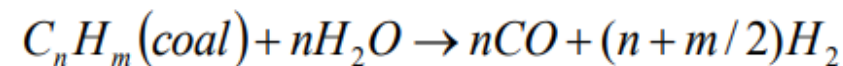
## ■ PLASMA REFORMING

- Method of production of carbon black and hydrogen gas
- High hydrogen yield and plasma catalysis consumes sufficiently low energy



## ■ COAL GASIFICATION

- Huge amount of clean hydrogen can be obtained
- Two products are carbon monoxide and hydrogen
- Three steps involved: 1) coal gasification; 2) water gas shift reaction; 3) CO<sub>2</sub> separation





Hydrogen production using water:

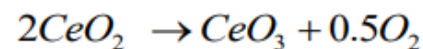
- **ELECTROLYSIS**

- Electrolysis of water generally breaks it into hydrogen and oxygen by passing electricity
- There are three main types of cell: a) Solid oxide electrolysis cells (SOEC'S) b) Polymer electrolyte membrane cells (PEM) c) Alkaline electrolysis cells (AEC'S)

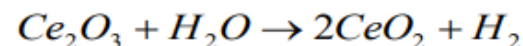
- **THERMOCHEMICAL CYCLE**

- Here heat energy (thermo) with chemical cycles is used to split water into hydrogen and oxygen components
- Thermo-chemical hydrogen production via 2-step using cerium oxides

a) Reduction



b) Hydrolysis



- **THERMOLYSIS**

- Hydrogen production by direct thermal decomposition of water
- Most effective hydrogen production in terms of production cost

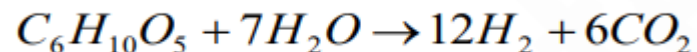






Hydrogen production using Biological processes:

- **BIO PHOTOLYSIS OF WATER USING ALGAE**
  - Same process as photosynthesis, but here it is used for hydrogen production
  - Two distinct photosynthetic systems: 1) water splitting and O<sub>2</sub> evolving system (PSII); and 2) photosystem (PSI)
- **FERMENTATIVE HYDROGEN PRODUCTION**
  - Fermentative ways, using organic compounds or biomass
  - Can be done by using direct bio photolysis through the green algae
  - Higher production of hydrogen in the day and night with a good production rate of microorganism and the supply of the reactant is very frequent
- **BIO CATALYZED ELECTROLYSIS**
  - Convert the biomass containing wastewater into valuable hydrogen gas
  - Electrochemically active microorganisms are used in an electrochemical cell

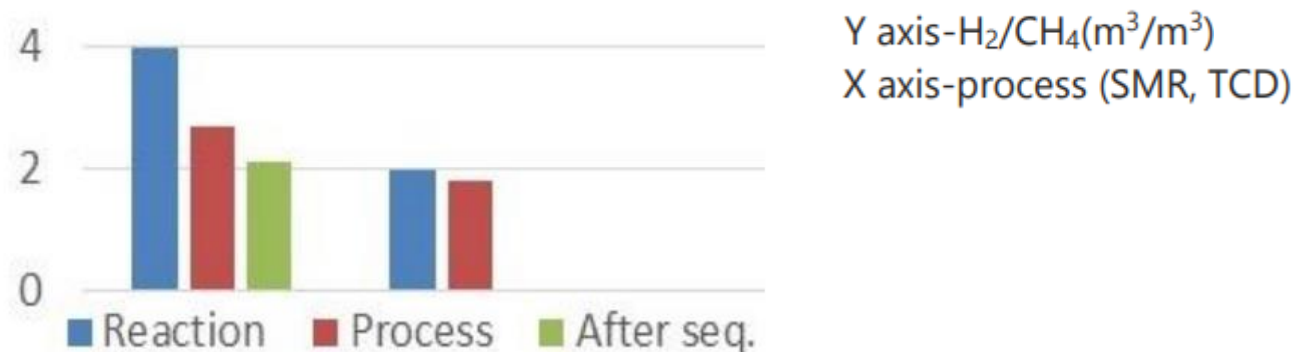






## ■ CRACKING OF METHANE/NG Vs SMR

- SMR contribute around 48% of world hydrogen production
- both consume a significant amount of energy in methane equivalent
- overall net efficiencies are same



Comparative assessment of net hydrogen yields from SMR and TCD process:

## ■ THERMAL CRACKING

- Thermal cracking of methane has been applied to produce carbon-rich hydrogen and carbon black
- Free radicals at the sites where molecular bonds are broken
- The cracking process could be arranged in a continuous process with the electric furnace as a heating source in combination with quartz micro reactor





## CONCLUSIONS:

- Methane cracking is a promising process to produce green hydrogen
- Different catalysts can be used, including Ni, Co, Fe, activated carbon, carbon black
- Carbon filaments are produced as a result of the reaction product of carbon diffusing through the metal catalyst particle, and then the diffusing carbon particle is deposited in filament form on the Ni/support interface
- In catalytic cracking, though the temperature requirement is less than that of the thermal process, for the latter case an extra amount of methane can be used for the production of extra energy.
- Encapsulating carbon and/or reactor space limitations are the primary deactivation causes
- Regeneration with steam and partial regeneration using air are effective in regaining the initial catalyst activity

## FUTURE ASPECTS:

- Methane cracking is not used industrially as not yet economically competitive with methane steam reforming.
- Active catalyst that can achieve high conversions, and remain stable
- Optimum operating conditions need to be realized
- A durable catalyst for fluidized bed applications needs to be developed
- New methods for carbon filament separation and improving the quality of the carbon deposited
- The catalyst needs to: provide high conversion; have excellent thermal and chemical stability; have high carbon capacity; last a long time; withstand attrition; be light weight.

