Production of CO_x-free Hydrogen and CNTs from Natural gas

WORLD FUTURE FUEL
SUMMIT & EXPO
International Conference & Exhibition on Future Fuel

IIT DELHI

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February - 2020.

Energy scenario: Hydrogen and CO_2 emissions

- **According to International Energy Agency, global energy demand will rise to 30% by 2040.**
- Three prominent options for sustainable production of carbon-free/CO_2 sequestration energy are:

De-carbonization of fossil energy (with CO_2 sequestration)

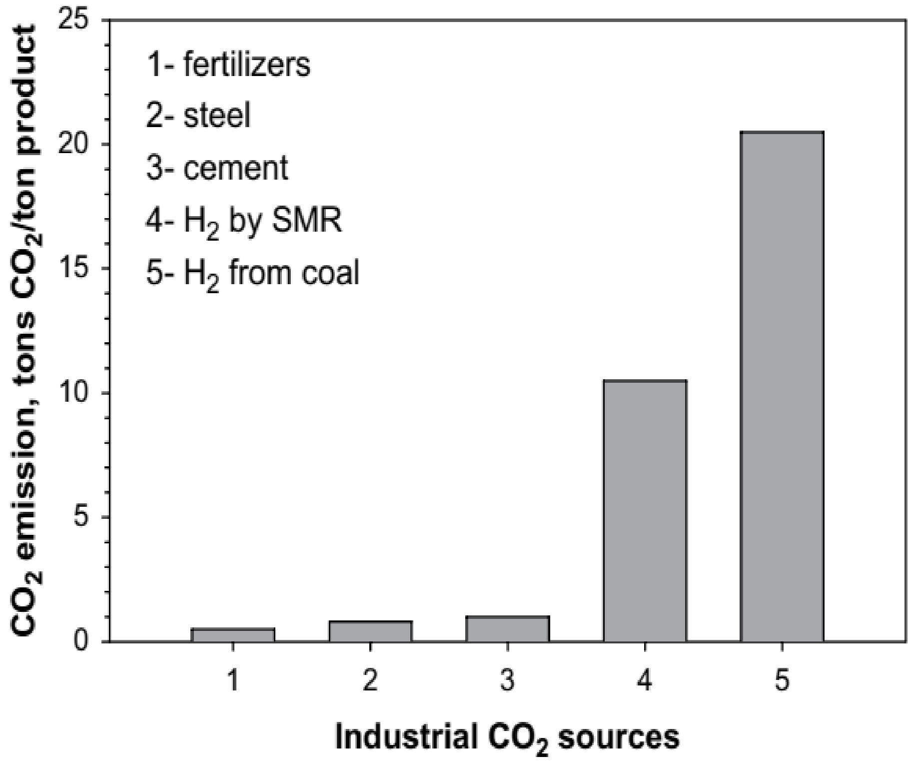
Renewable energy resources.

Nuclear energy

- **Steam Reforming (SRM)**
- **Partial Oxidation (PO)**
- **Thermo-Catalytic Decomposition (TCD)**

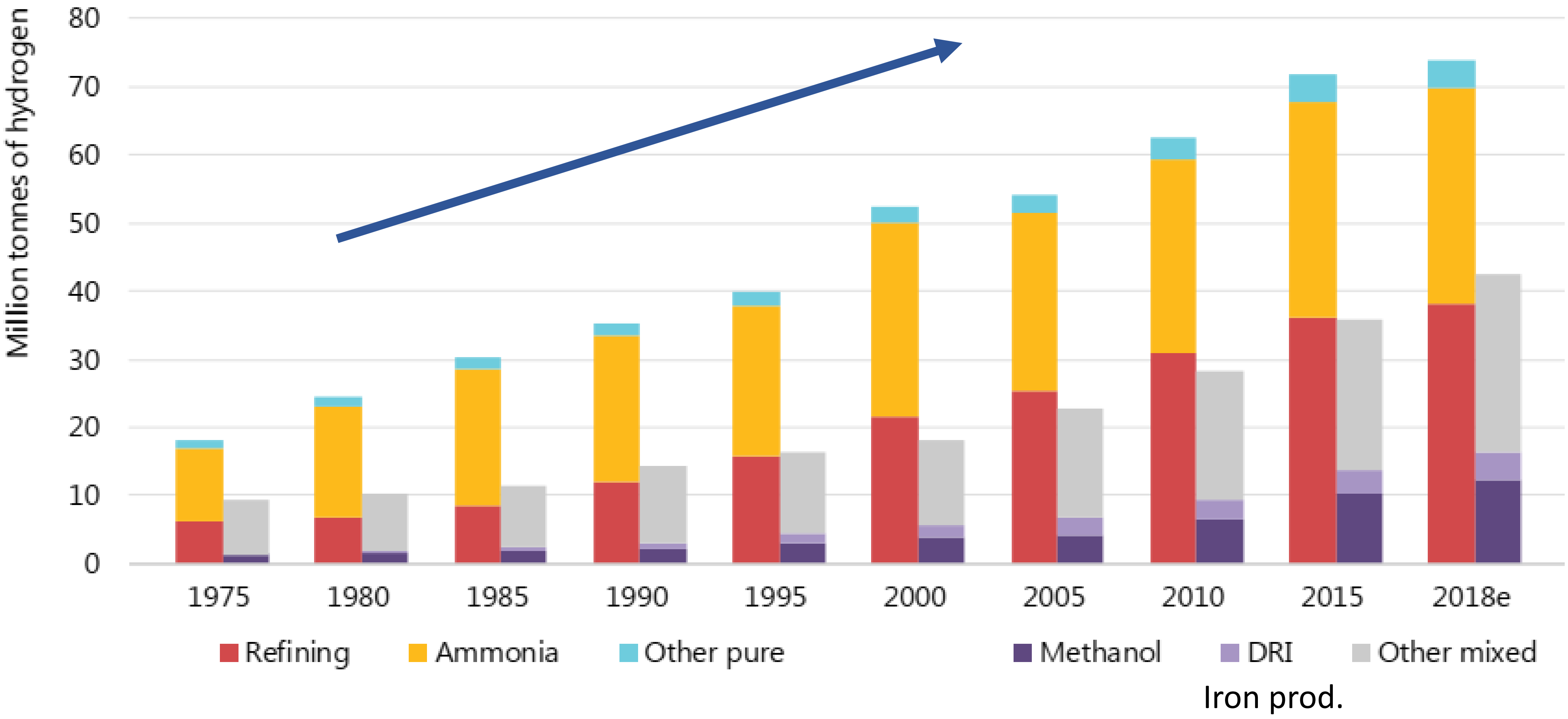
→ **Hydrogen + Carbon** → **CO_2** / **CNTs**

CO_2 emission from various industries



Hydrogen has been identified to be one of the few potential energy carriers in the low carbon economy.

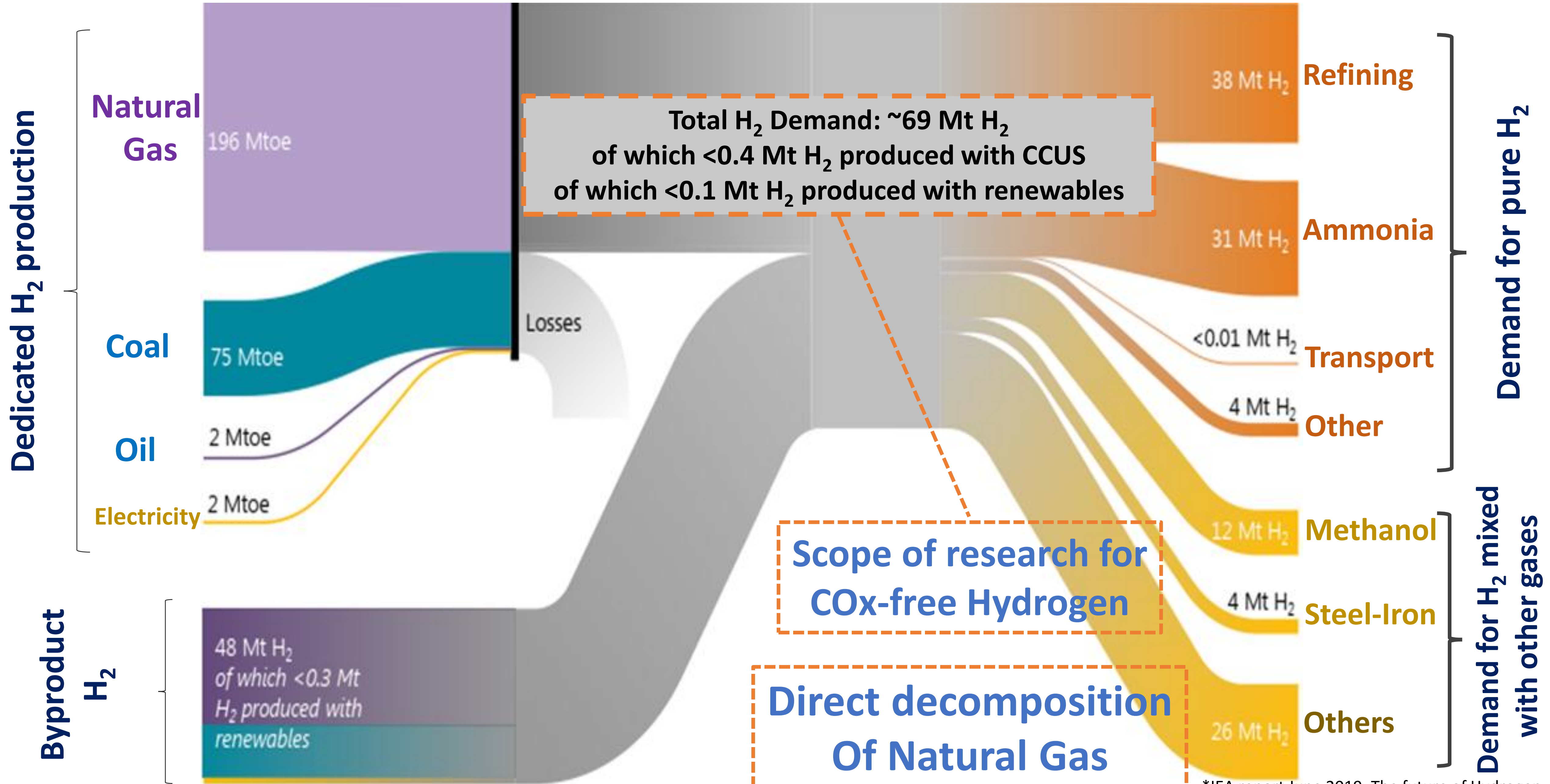
Global Annual demand for Hydrogen



Demand for Hydrogen has grown more than threefold since 1975

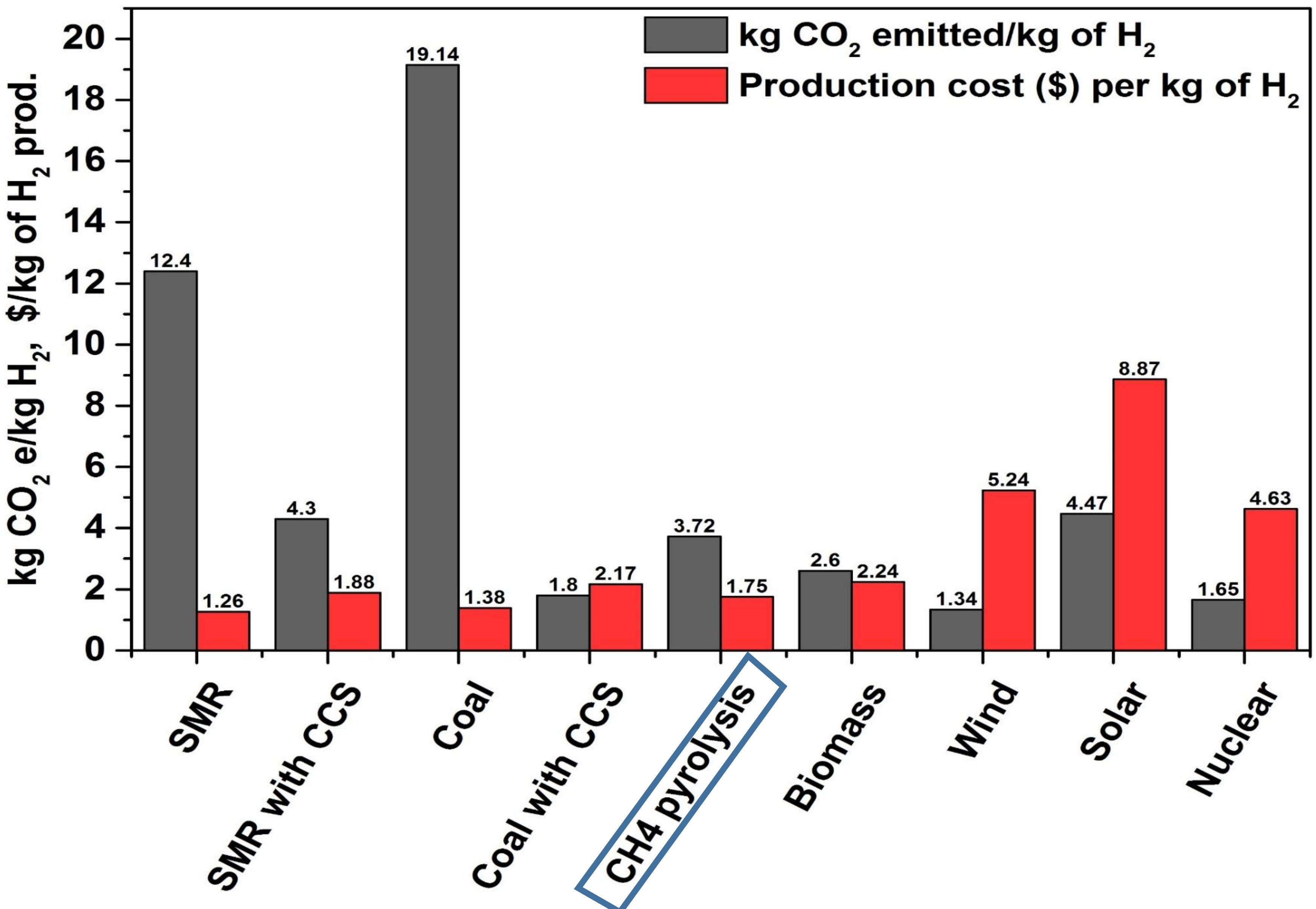
*IEA report June 2019, The future of Hydrogen

Hydrogen demand and usage



*IEA report June 2019, The future of Hydrogen

H_2 production cost using different technologies



- Natural gas pyrolysis is greenest process (considering both H_2 production price and CO_2 emission) among all the processes.
- The production cost of the Hydrogen can be lowered by increasing carbon selling price.

H_2 production cost (with CCUS)
: 1.5-2.5 USD/kgH_2

Parkinson et al, Energy Env. Sci. 2019, 12,19

Need for Natural gas decomposition

Steam Methane Reforming

- $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$
- $\Delta H°_{298K}$ =39.43 kcal/mol CH_4
- **13.7 kg CO_2/kg of H_2 production**

Major drawbacks of SRM:

- CO_2 capture and sequestration
- PSA unit
- Additional cost

Catalytic Decomposition of Methane

- $CH_4 \rightarrow C + 2H_2$
- $\Delta H°_{298K}$ = 18.06 kcal/mol CH_4
- **3.73 kg C/kg of H_2 production***
- **747 g of C/kg of methane***

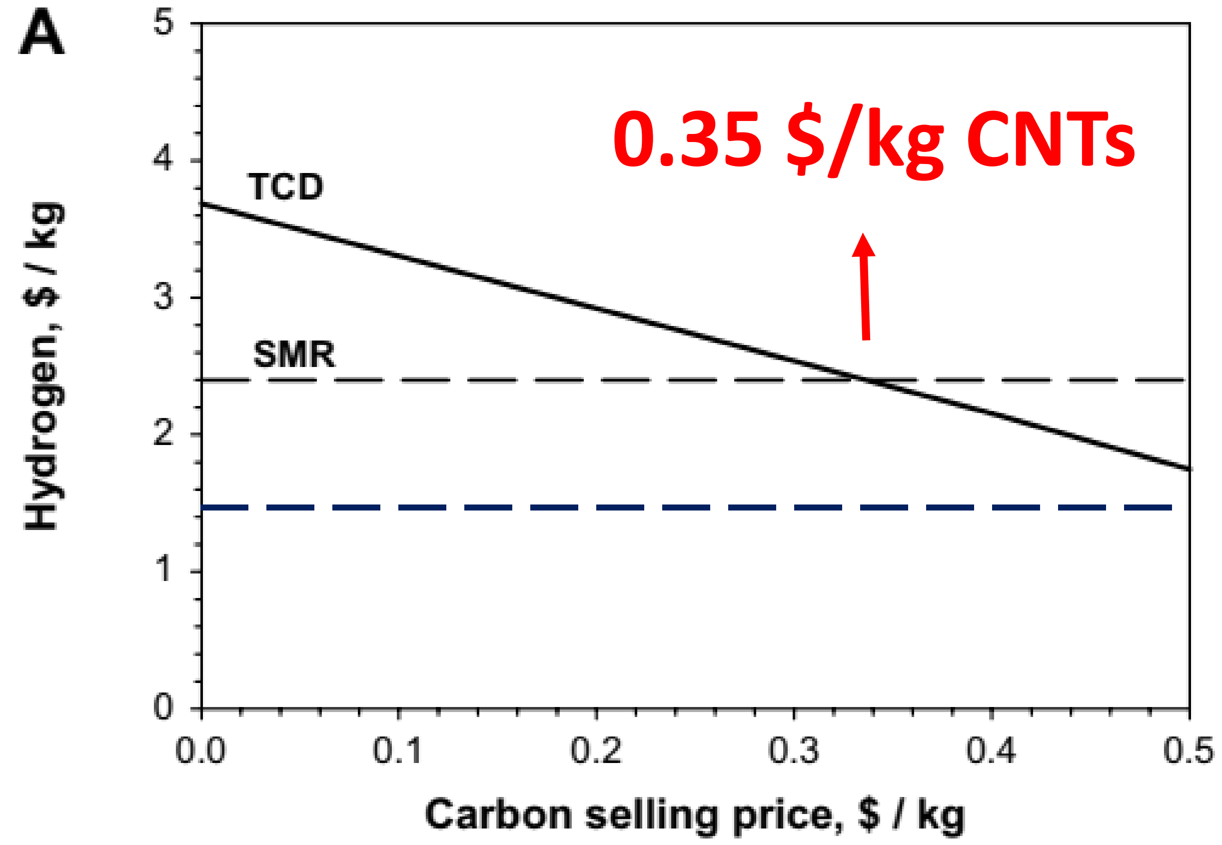
Advantages of Direct decomposition

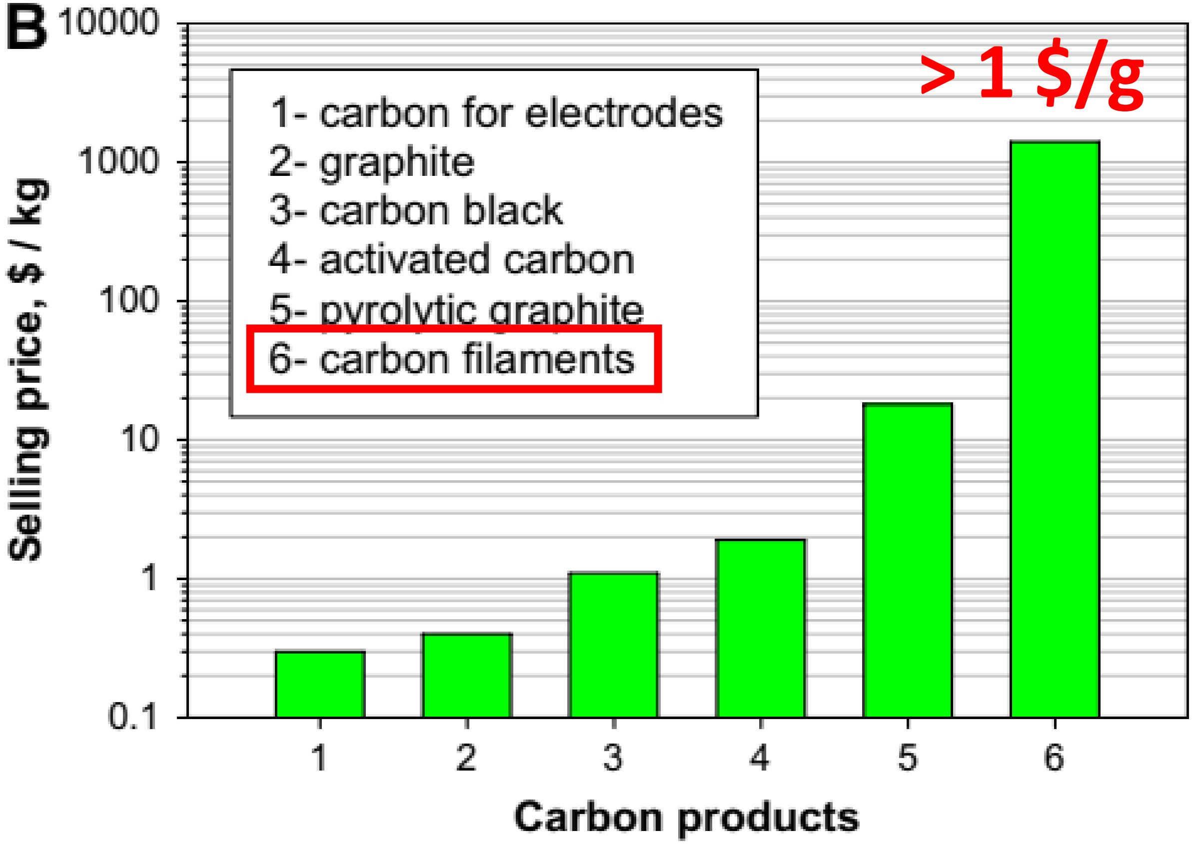
- **Produced carbon is in the form of CNTs which is a valuable by-product**

Total CO_2 emissions from CO_2 sequestration could potentially reach 0.25 kg CO_2 per kg of sequestered CO_2.

* through stoichiometry

Economics of direct decomposition: Based on price of the CNTs





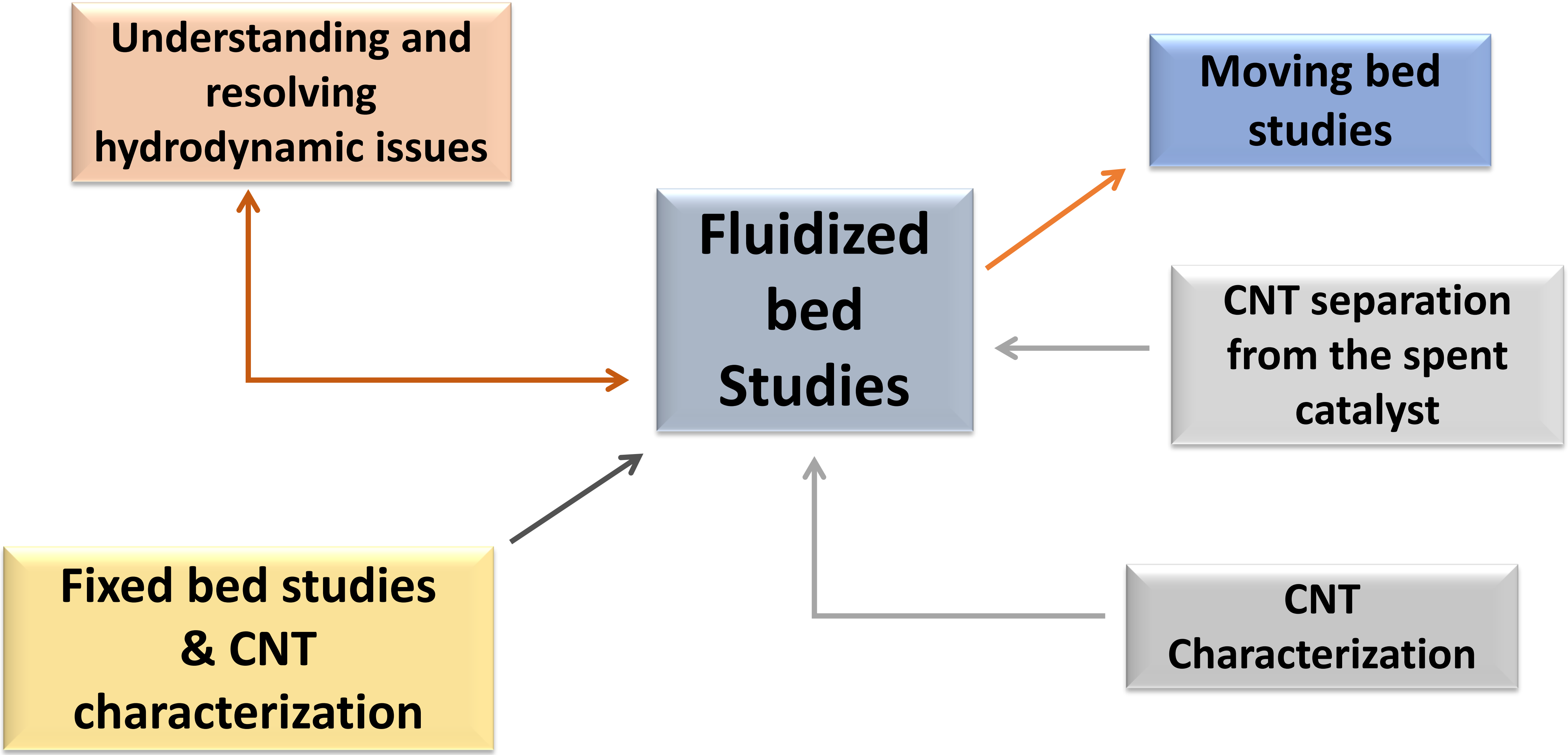
Hydrogen production cost is a function of CNTs selling price.

TCD process becomes competitive with SMR at a carbon selling price of about 0.35 $/kg carbon. Current price of carbon filament/CNTs (TCD by-product) is > 1000$/kg.

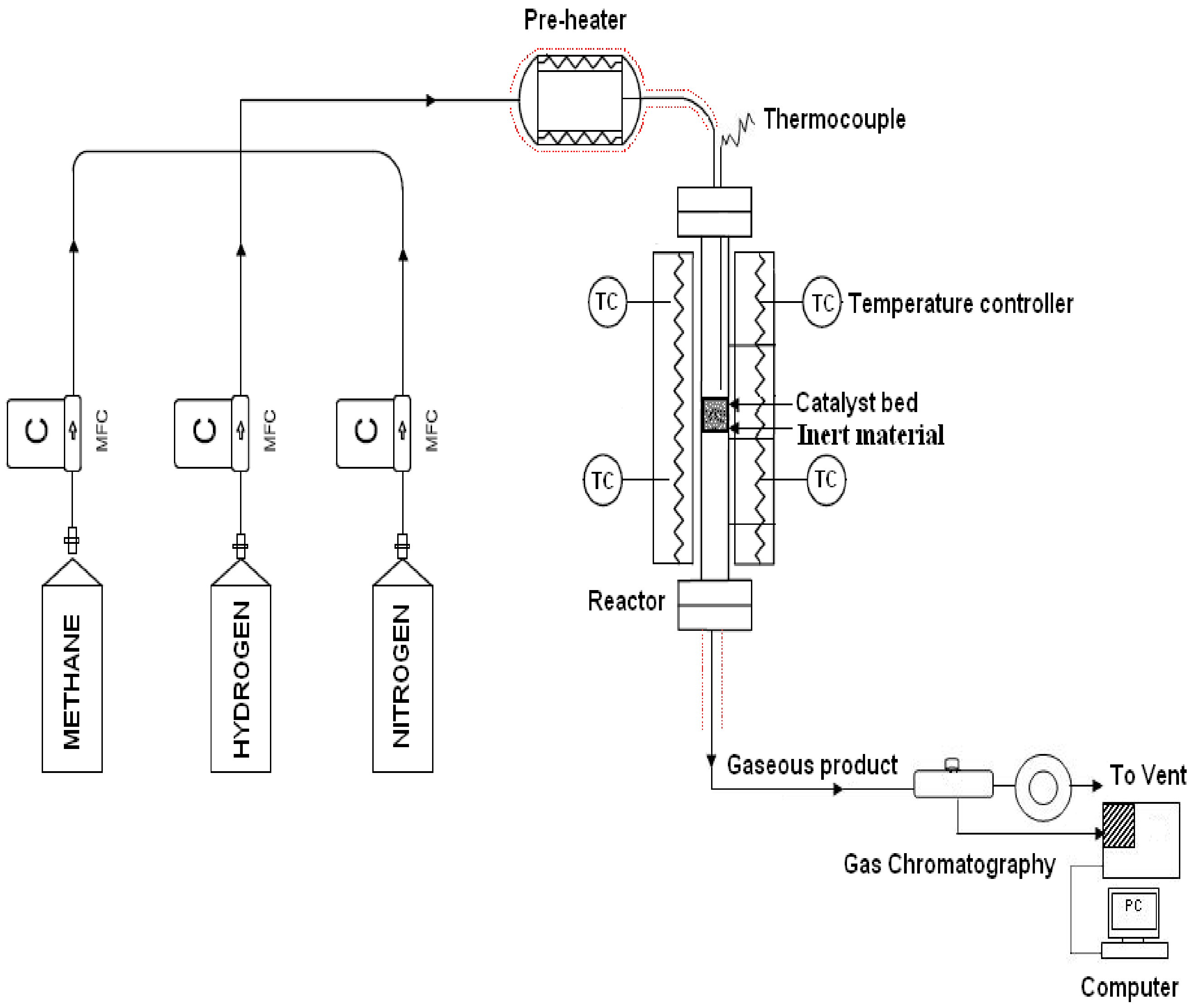
The CNTs produced in TCD process is sulfur and ash free, which could be marketed at even higher selling price

*Muradov and Veriroglu, IJHE, 2008, 33, 6804

Overall approach



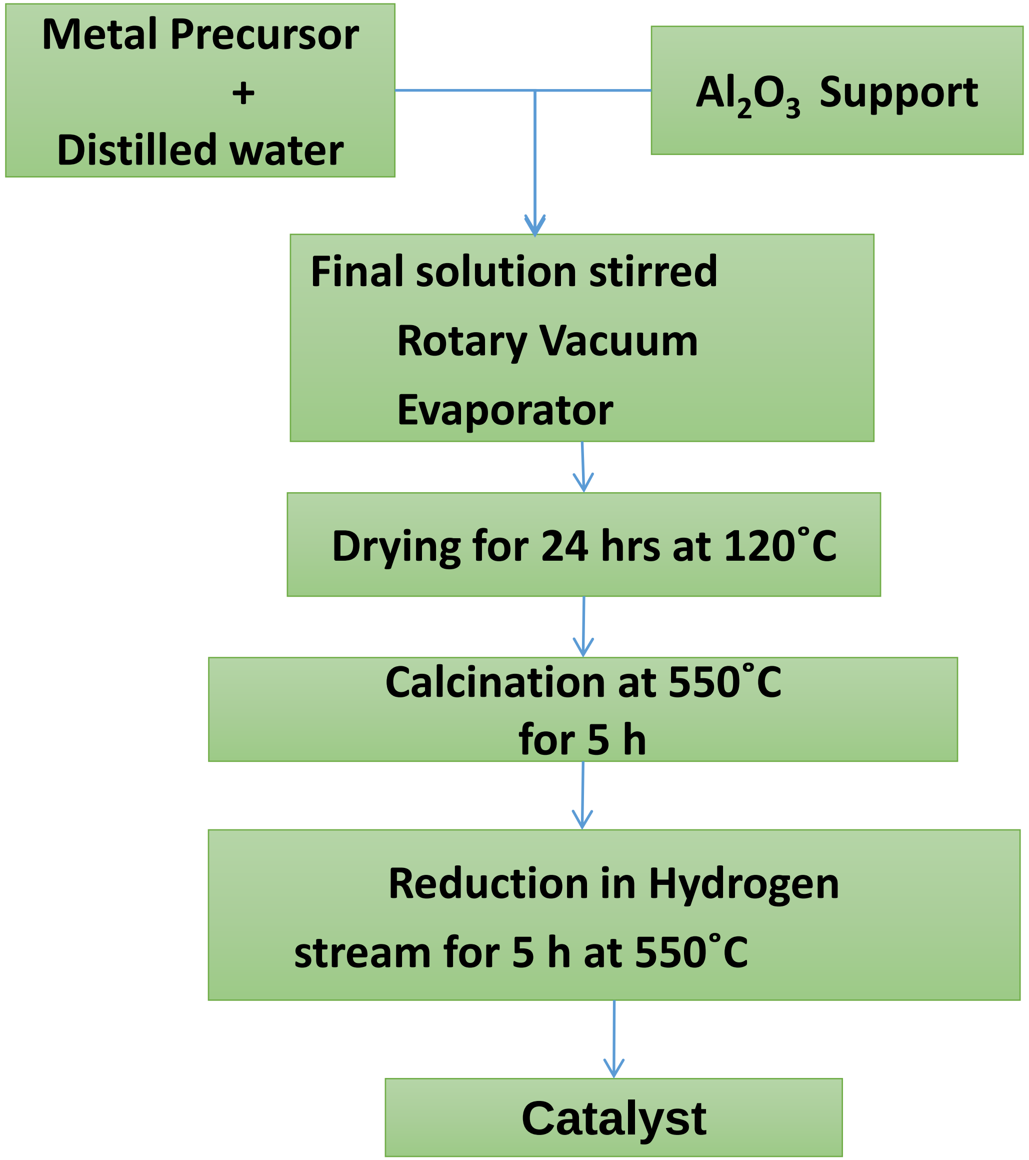
Schematic diagram of Experimental Setup



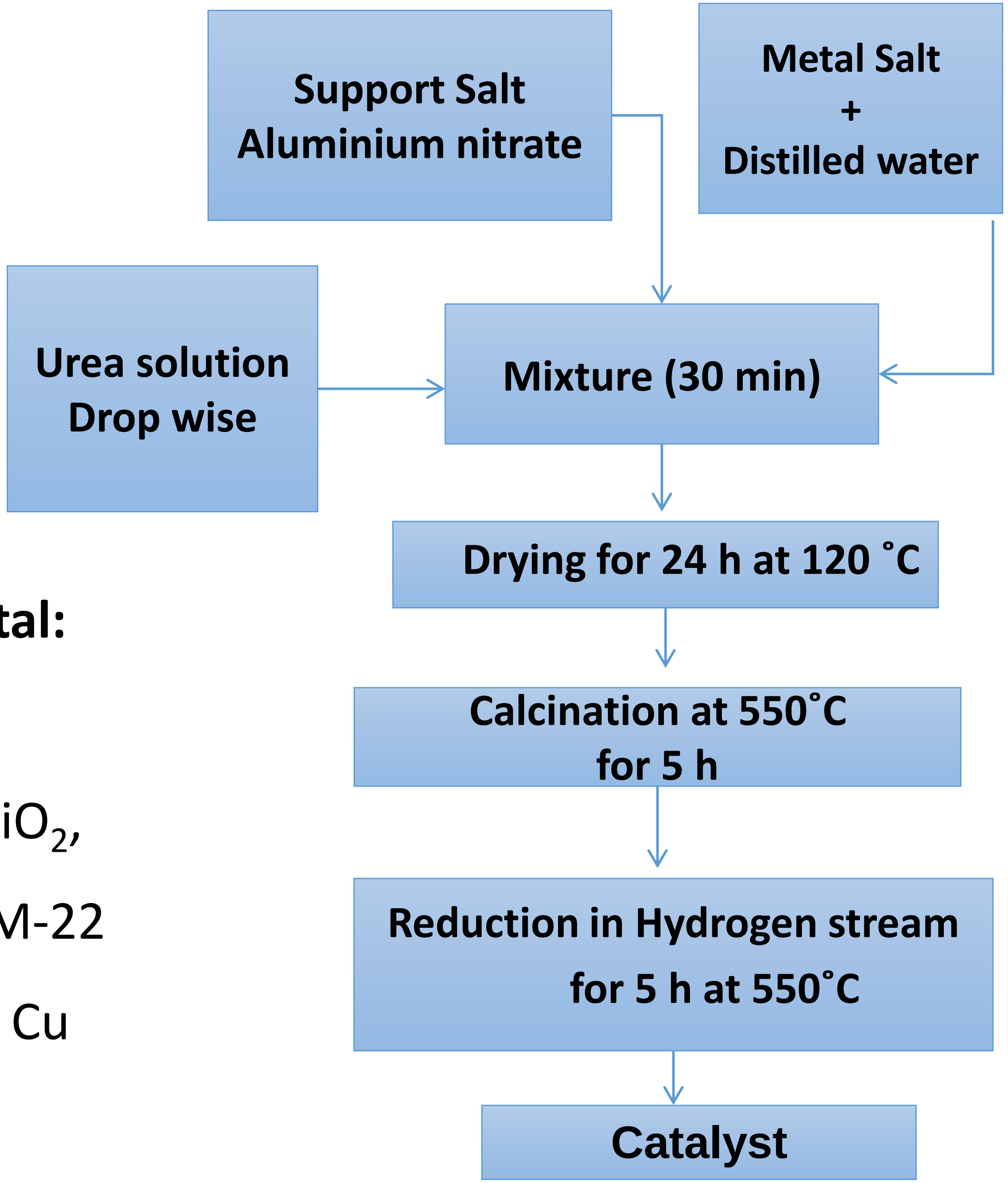
Tubular fixed Quartz Reactor, L-600 mm, ID-19 mm

Parameters	Range
Temperature (°C)	550-800
Pressure (atm.)	1
Run Time (h)	2-75
Weight of the catalyst (g)	0.5-2.0
Flow rate of Nitrogen (mL/min) GHSV (mL/h.g_{cat})	10-200 (600-12000)
Flow rate of Methane (mL/min) GHSV (mL/h.g_{cat})	10-200 (600-12000)

Catalyst preparation: Wet Impregnation (L) Co-Precipitation (R)



- **Active metal:** Ni, Co, Fe
- **Support:** SiO_2, Al_2O_3 ,MCM-22
- **Promoter:** Cu and Zn



Comparative study of catalysts: H_2 yield and Carbon quality

Catalysts	Preparation method	Metal loading (wt%)	Max.CH_4 conversion (%)	Maximum H_2 yield (%)	Max CNT yield (%)*	CNT structure
Fe/SiO_2	W.I.	30-70	5-9	4-8	-	Amorphous
Fe/Al_2O_3	W.I.	30-70	7-15	6-13	-	Amorphous
Co/SiO_2	W.I.	30-70	16-62	15-60	428	Multiwalled
Co/Al_2O_3	W.I.	30-70	18-67	16-64	460	Helical
Ni/SiO_2	C.P.	30-70	17-70	16-68	507	Multiwalled
Ni/SiO_2	W.I.	30-70	22-77	20-75	592	Multiwalled
Ni/MCM-22	W.I.	30-70	26-70	25-68	720	Multiwalled
Ni/Al_2O_3	C.P.	30-70	31-75	30-73	811	Multiwalled
Ni/Al_2O_3	**W.I.**	**30-70**	**32-80**	**31-78**	**991**	**Multiwalled**

Wet-impregnated Nickel catalyst provides high CH_4 conversion and Multi-walled CNTs

(T = 750 °C, P_{CH4} = 0.25, $GHSV_{CH4}$= 1800 ml/h.g_{cat}, Wcat = 1.0 g)

- S. K. Saraswat, **K. K. Pant**, J. of Env. Chemical Engg. 2013, 1, 746.
- S. K. Saraswat, **K. K. Pant**, J. of Natural Gas Science and Engg. 2013, 13, 52.

Effect of promoters

Catalyst A:

60% Ni/Al_2O_3

Catalyst B:

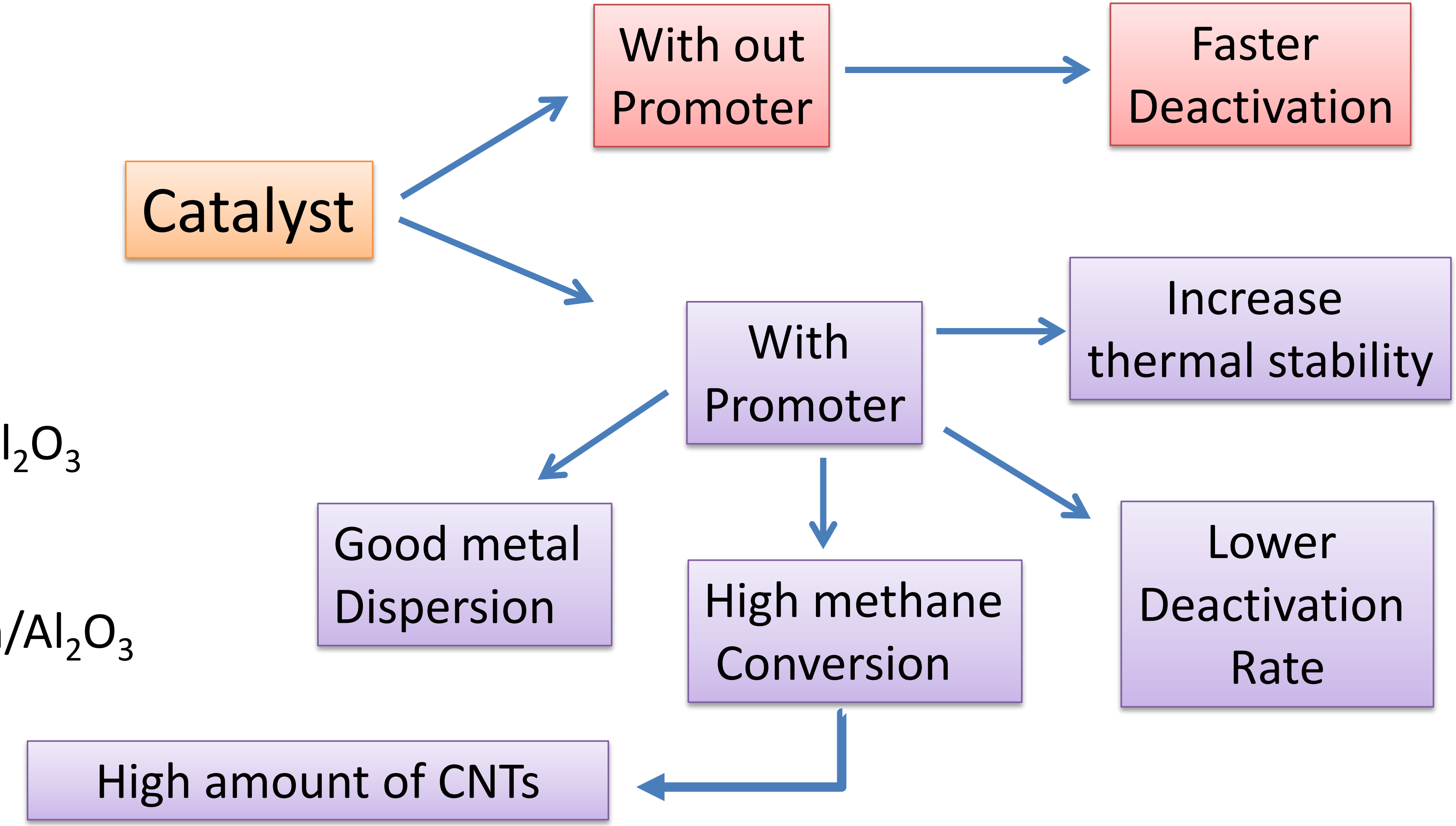
60% Ni-5% Cu/Al_2O_3

Catalyst C:

60% Ni-5%Cu-5%Zn/Al_2O_3

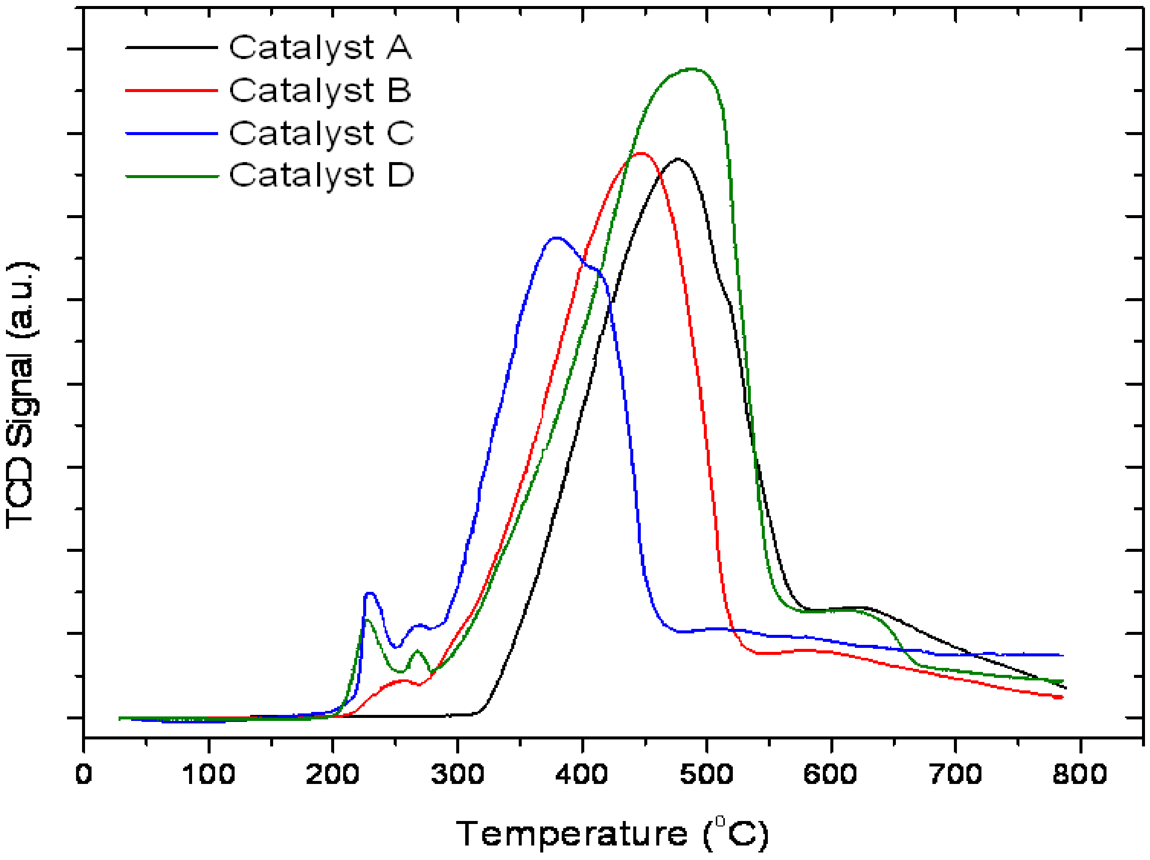
Catalyst D:

60% Ni-10%Cu-10%Zn/Al_2O_3

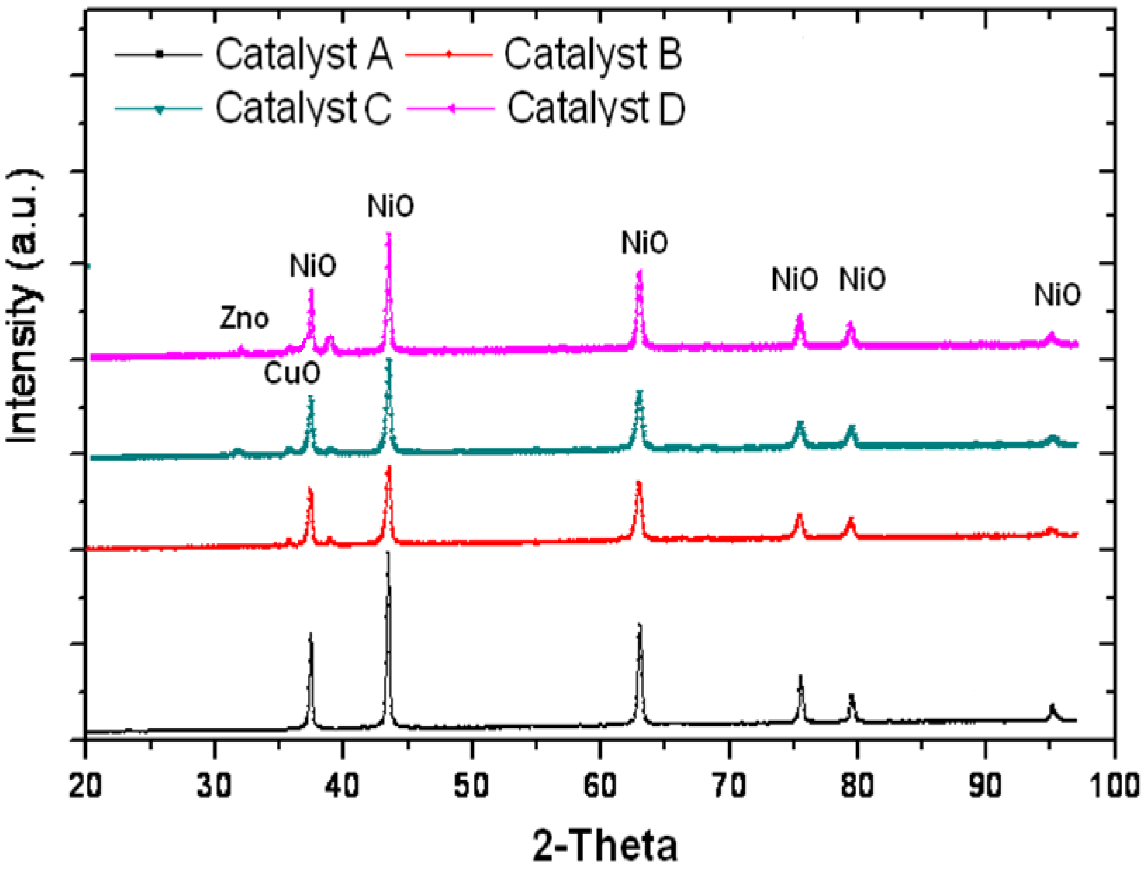


☞ **Interactions between the metal and the support leads to increase catalyst performance**

TPR and XRD analysis



Temperature programmed reduction of fresh catalyst



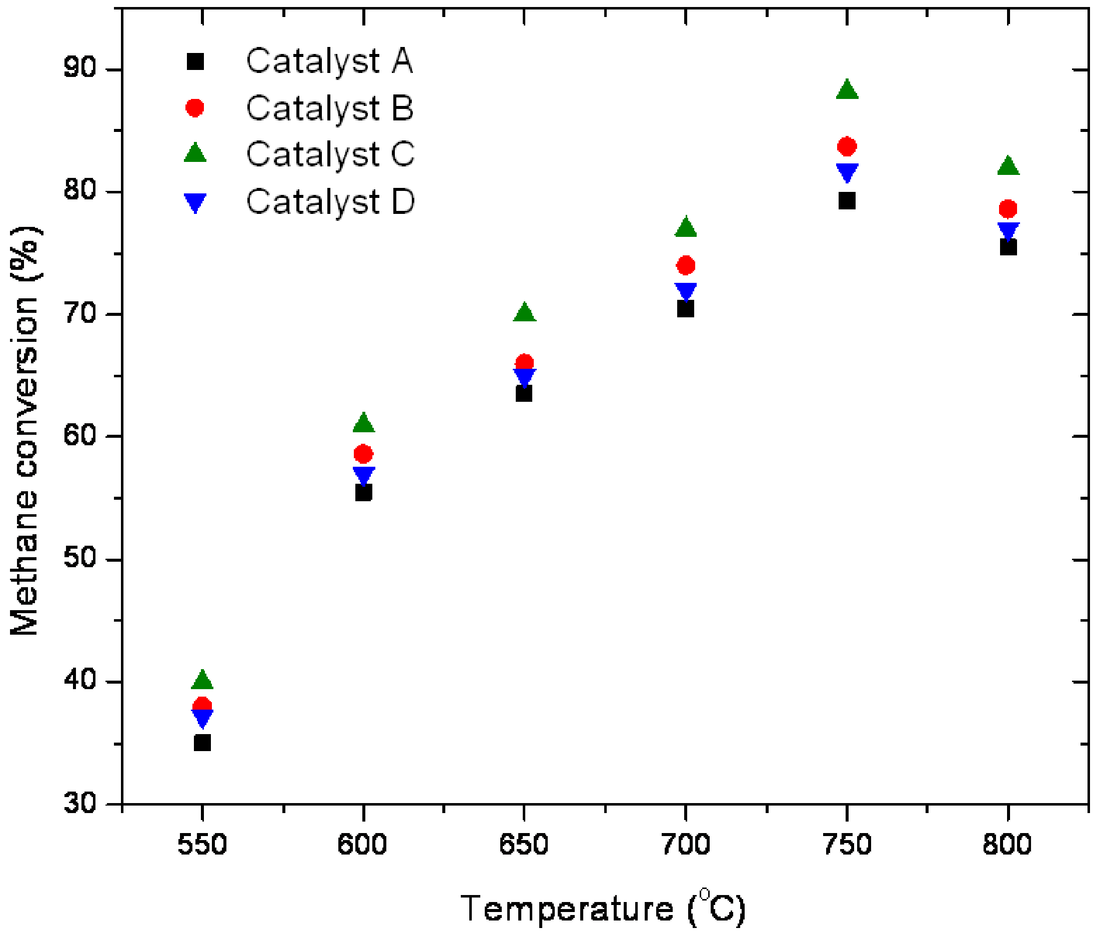
X-Ray diffraction of fresh catalyst

- Decreased reduction temperature due to addition of promoters
- Cu promotes the reduction of NiO.

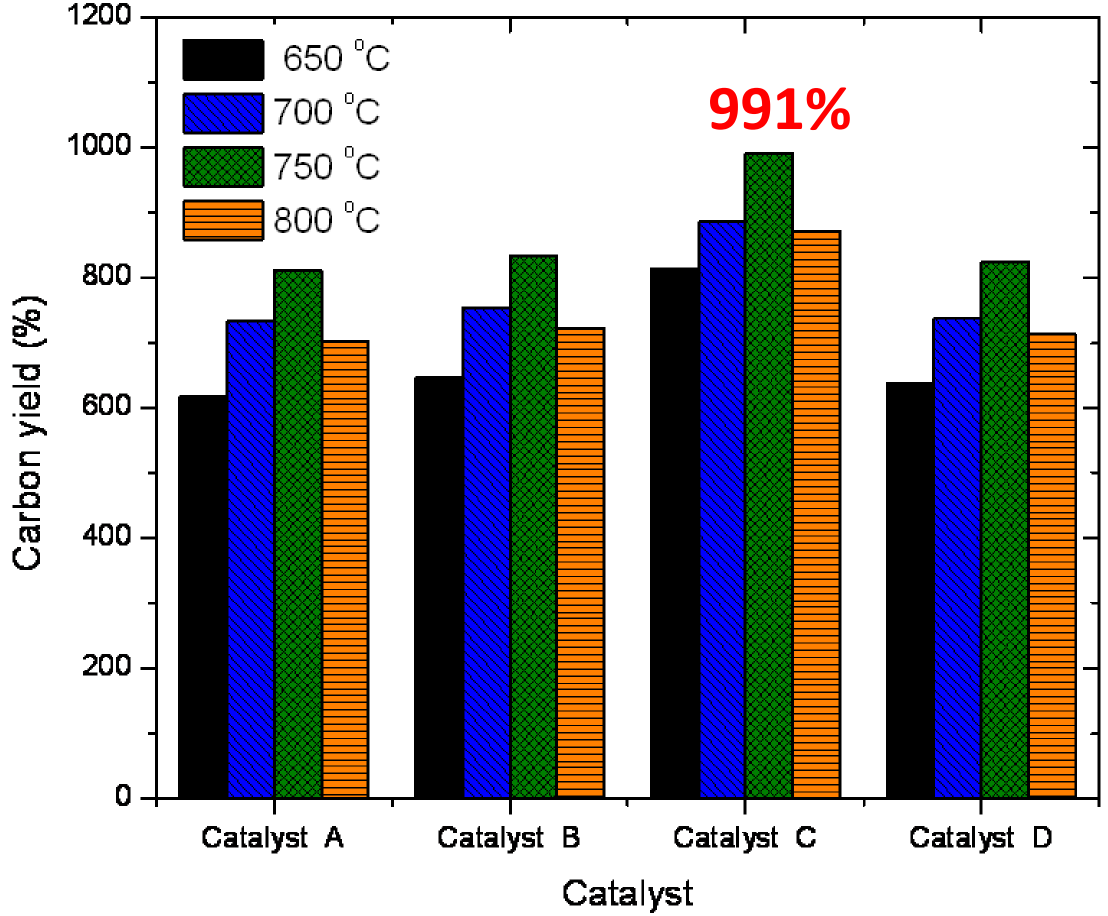
- XRD confirms the presence of NiO, CuO and ZnO spices

(Calcination temp. 550 ˚C)

Effect of promoters on CH_4 conversion



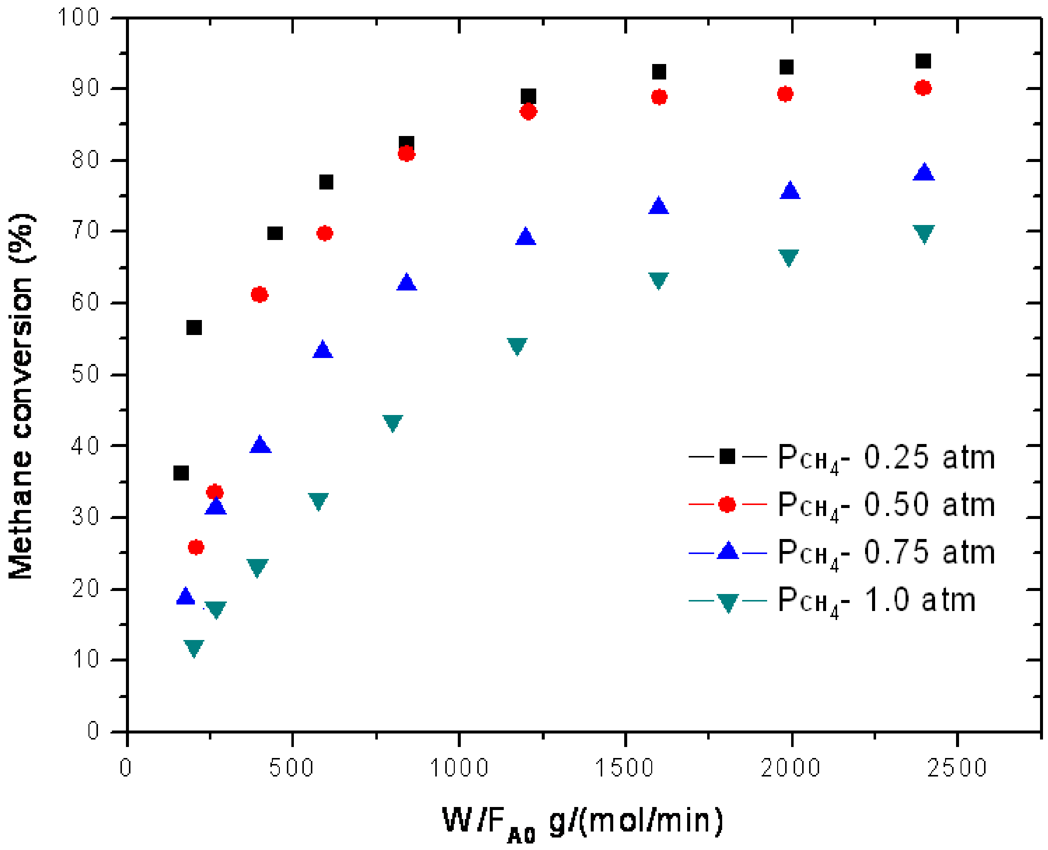
Effect of reaction temperature on carbon yield



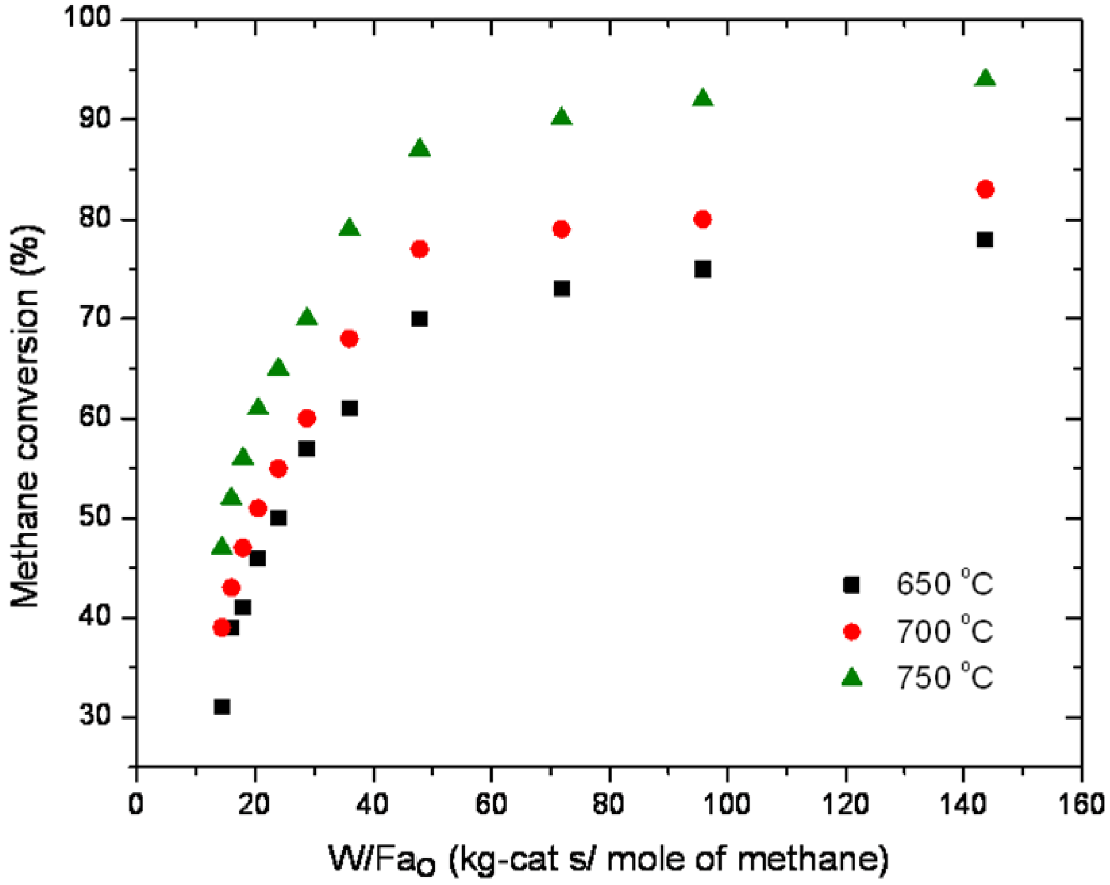
60% Ni-5%Cu-5%Zn/Al_2O_3 (catalyst C): highest methane conversion and carbon yield (991%)

S. K. Saraswat, **K. K. Pant**, Int. J. Hydrogen Energy 2011, 36, 13352

Effect of partial pressure



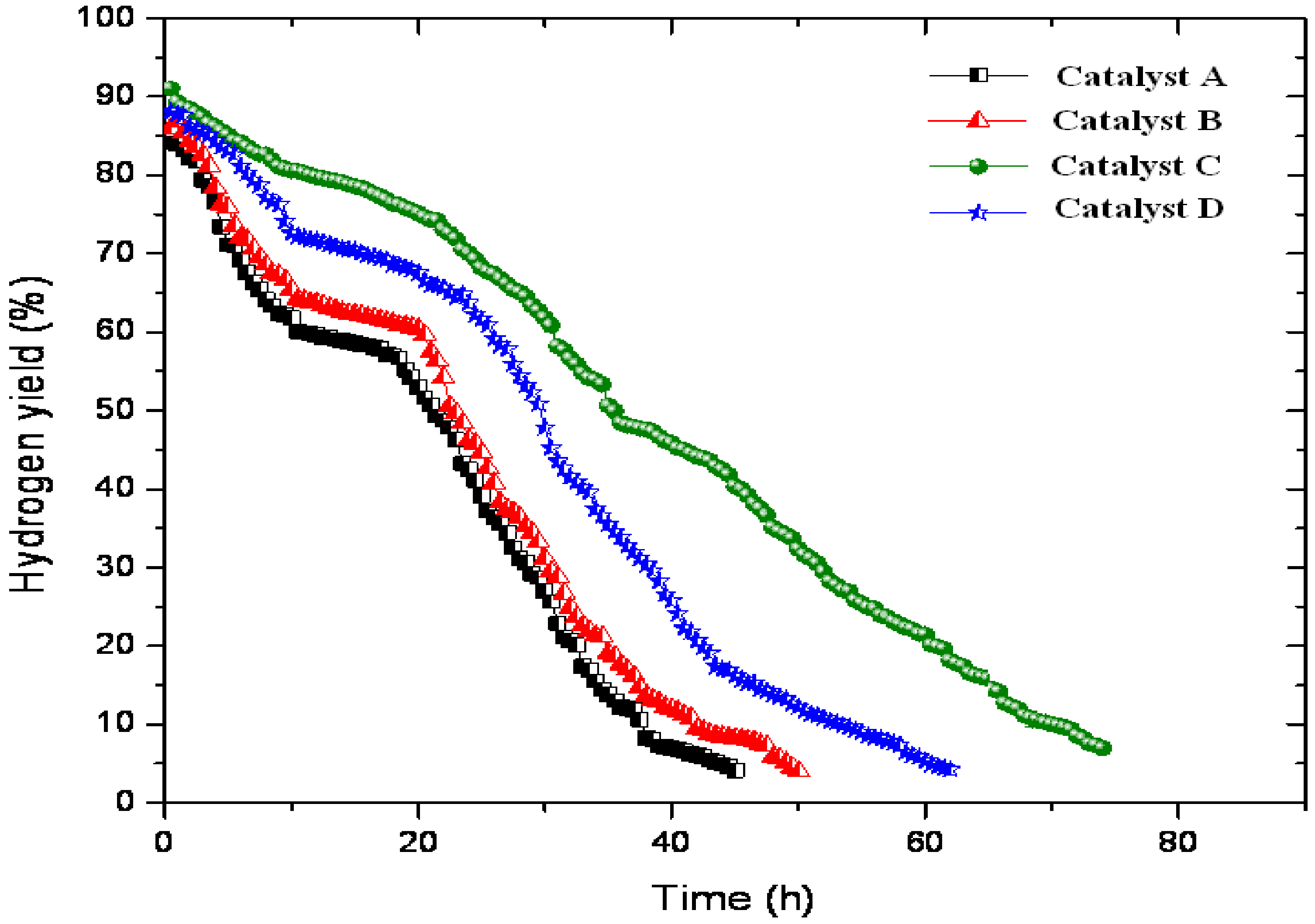
Effect of W/F_{A0} and temperature



Maximum conversion (93%) and hydrogen yield (91%) was obtained for catalyst C (60% Ni-5%Cu-5%Zn/Al_2O_3) (space time of 143.7 kg-cat s/mole of methane and P_{CH4} 0.25 atm)

- Pant K. K., et al. **WO2014188439 A1, CA2913277A1, US2016029424**.

Effect of run time on hydrogen yield



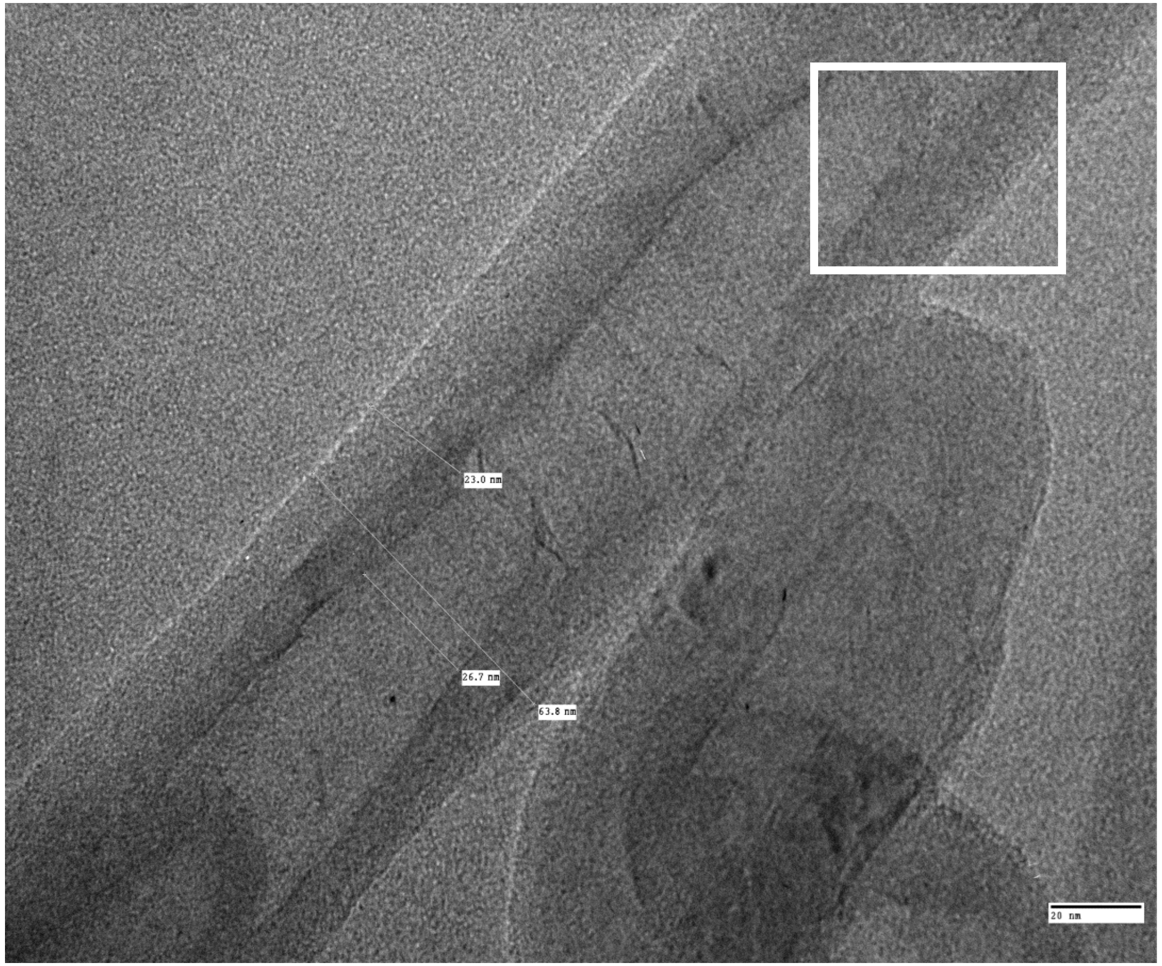
Catalyst C:

60%Ni-5%Cu-Zn/Al_2O_3

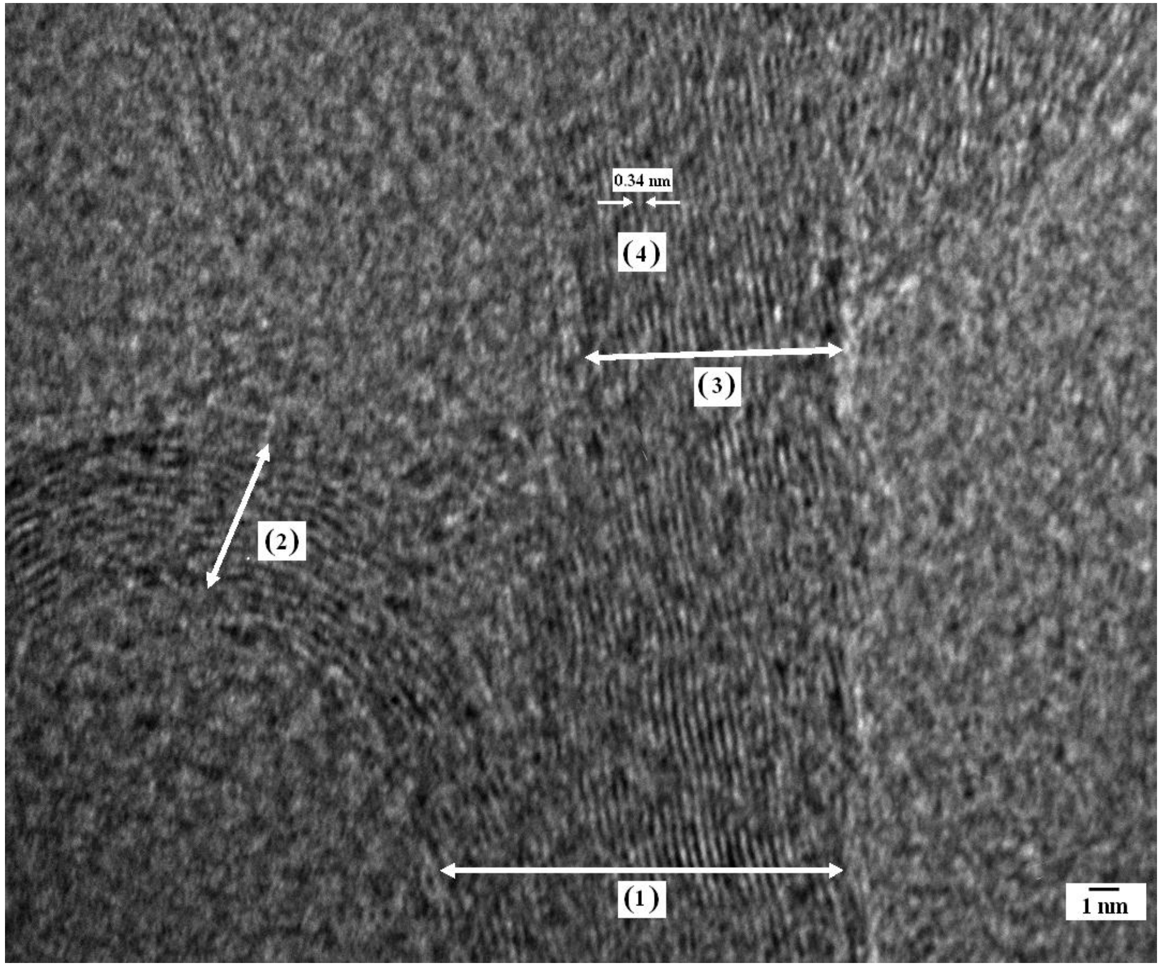
Deactivation time=72 h

Reaction temp. 750 ^oC, GHSV- 600 ml/h.g_{cat}

TEM analysis of produced CNTs

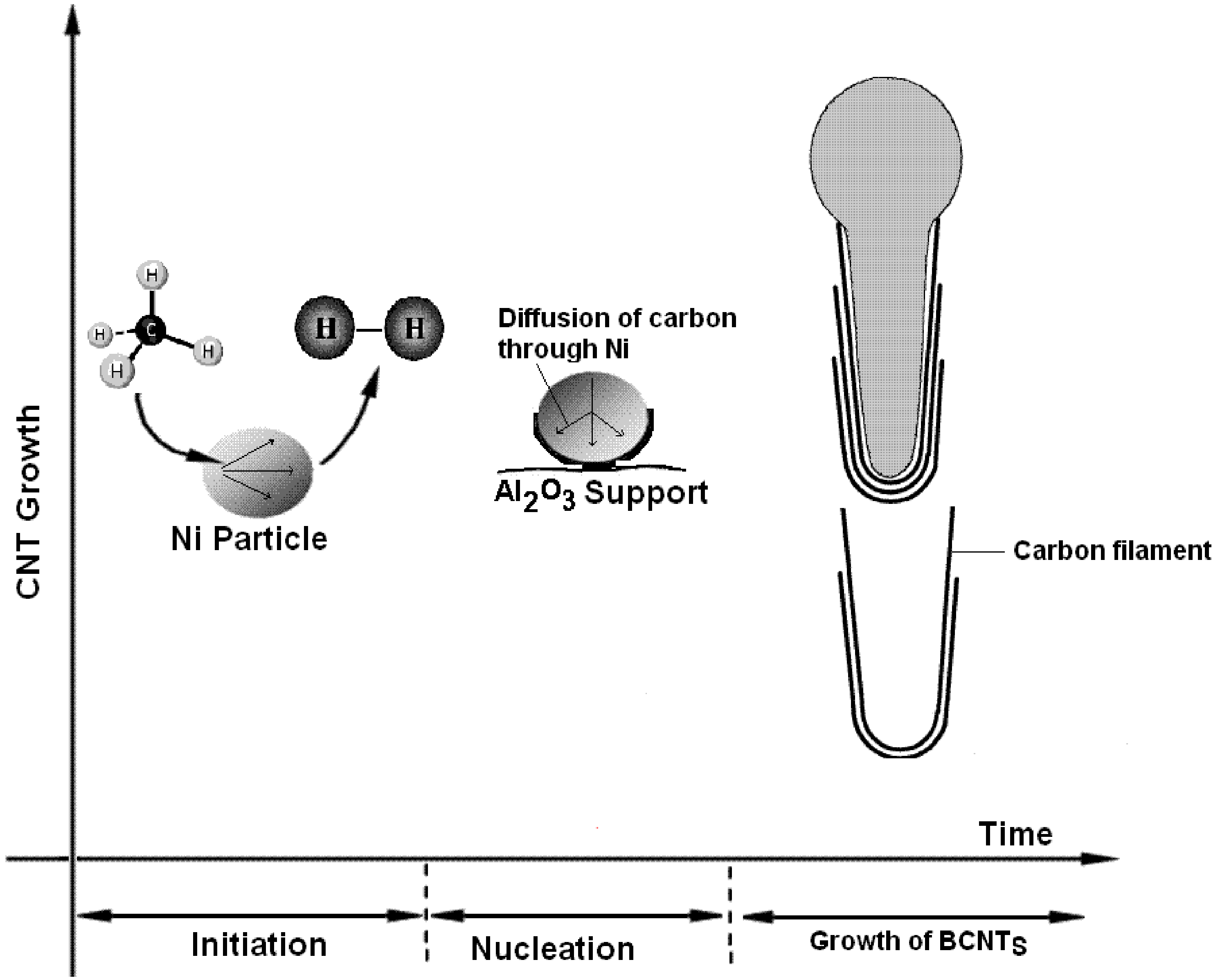


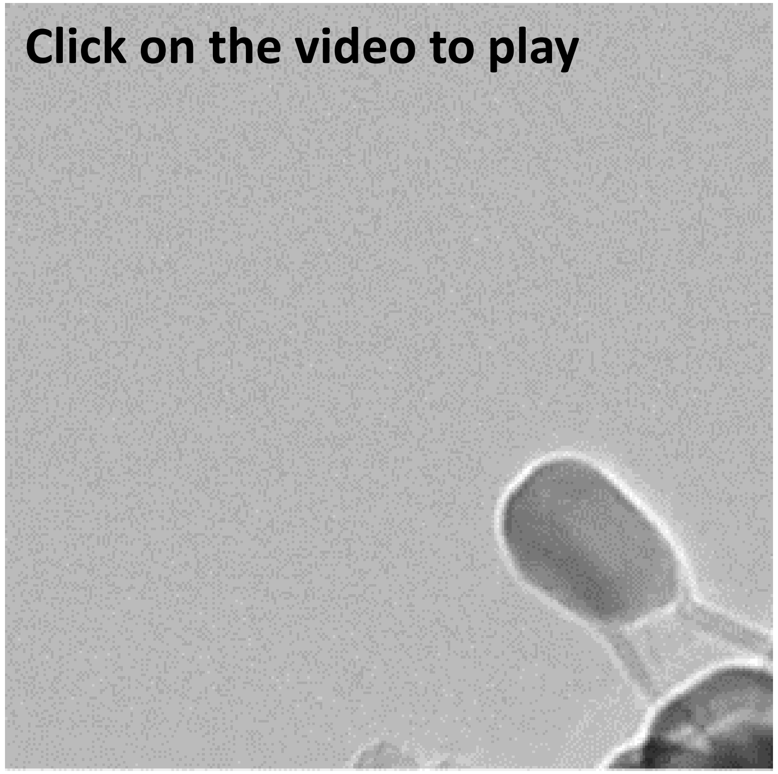
HRTEM Analysis
60%Ni-5%Cu-5%Zn/Al_2O_3 catalyst (C)
ID =26.7 nm, OD = 63 nm



Arrow 1: Wall graphite layer ,
Arrow 2: compartment graphitic,
Arrow 3: after compartmentalization
Arrow 4: graphite plane distance (0.34 nm)

Schematics of mechanism of CNT formation





CNT growth captured by insitu TEM

Why Fluidized bed reactor ? : Scale-up aspect

- Catalyst gradually deactivates due to accumulation of carbon on the catalyst surface. So, regeneration is required.

- Difficult to maintain continuous carbon removal in the fixed bed reactor.

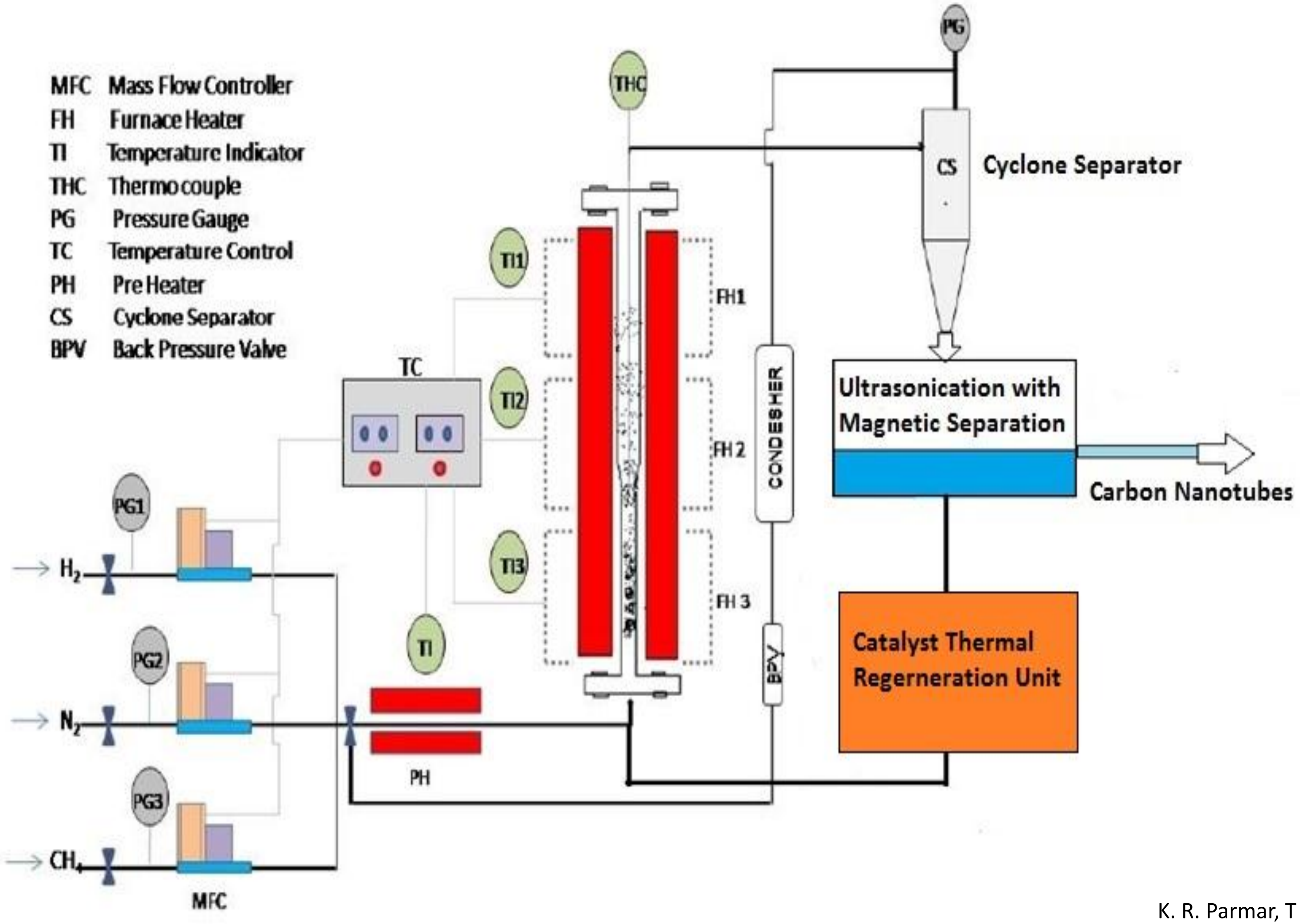
- Solid carbon deposits causes severe fouling of the reactor and increase the pressure drop.

- Difficulty in scale-up

- In case of regeneration by air, exothermic regeneration step drives endothermic decomposition step. However, air regeneration leads to sintering of catalyst.

- So, fluidization bed reactor is the best option for methane decomposition which can facilitate not only continuous operation but also CNT separation and regeneration.

Lab Scale Fluidized Bed Reactor (FBR)



Reactor Conditions:

T = 750 ˚C

60% Ni-5%Cu-5%Zn/Al_2O_3

U0 = 2 Umf = 4.2 cm/sec

Total flow = 200 ml/min

P_{CH4} = 0.25

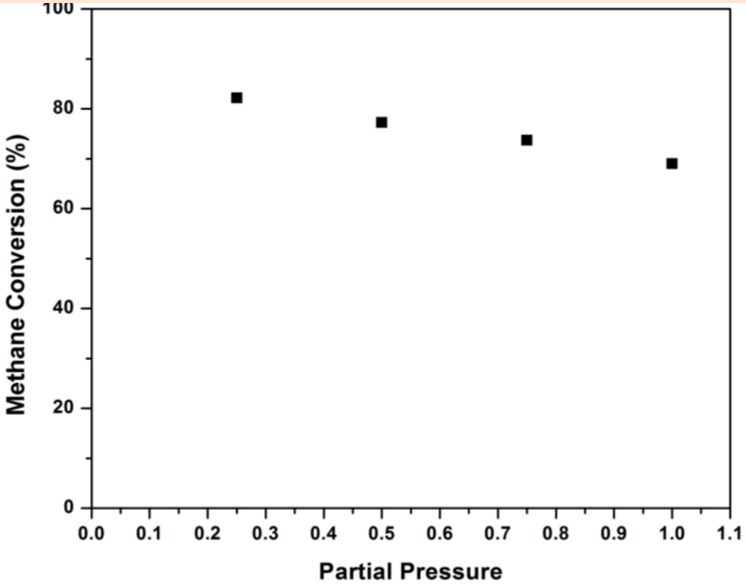
Catalyst wt. = 5 g

Reactor ID = 12 mm

$GHSV_{CH4}$ = 600 ml/h gcat.

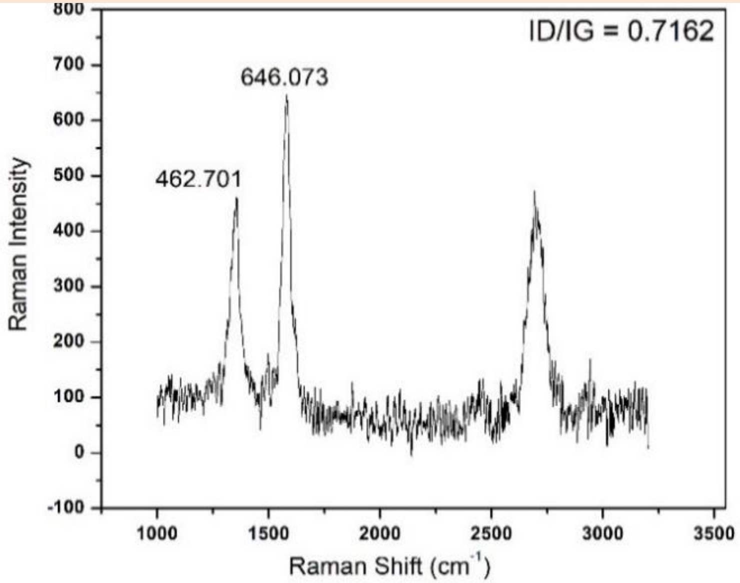
K. R. Parmar, T Dora, **K. K. Pant**, J. Hazardous Materials 2019, 375, 206

Effect of CH_4 partial pr. on CH_4 conversion



- More than 90% initial methane conversion was achieved.
- Highly structured CNTs (ID/IG = 0.71)
- At this conversion level, 1 kg/h CH_4 (feed) pilot plant can produce approx. 650 g CNTs/h.

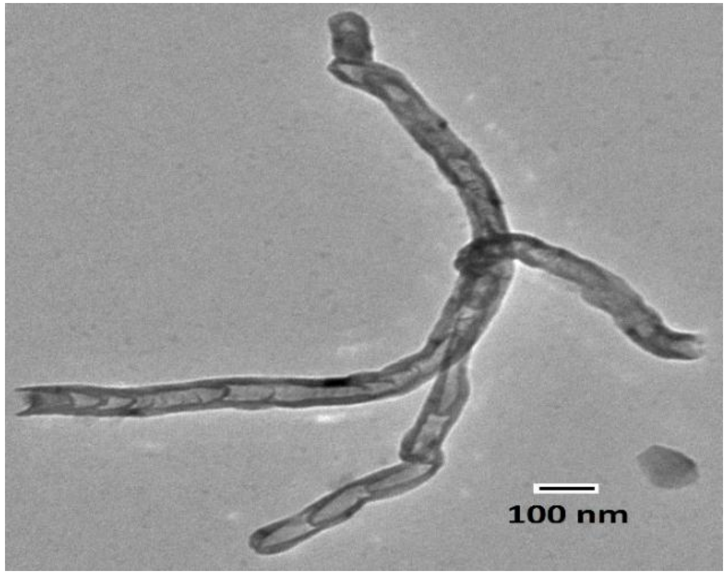
Raman spectra of produced CNTs in FBR



FESEM analysis of produced CNTs in FBR

- Bamboo shaped multi-walled nanotubes.
- High Length to Diameter ratio
- Uniform size with less structural deformities

TEM analysis of produced CNTs in FBR



Summary

- Among the catalysts prepared, 60%Ni-5%Cu-5%Zn/Al_2O_3 catalyst prepared by wet impregnated method was found to be most promising, for the production of COx-free hydrogen and carbon nanofibers.
- The maximum **methane conversion** over 60%Ni-5%Cu-5%Zn/Al_2O_3 was **94%** (**92.7% hydrogen yield**) at 750 ^{o}C.
- Doping of copper and zinc promoter significantly increases the activity of Ni, **promotes the nano-carbon growth rate on the surface, decreases the binding energy of Ni and reduces the deactivation process.**
- TEM and HTREM images confirms the high purity bamboo-shaped structure of CNTs produced over 60%Ni-5%Cu-5%Zn/Al_2O_3 catalyst with **outer and inner diameter in the range of 60-65 nm and 25-30 nm and 2-3 μm in length.**

Acknowledgement

Kaushal Parmar

Dr. Sushil Saraswat

Collaborators/Partners

- Hindustan Petroleum corporation limited (HPCL)
- Centre for High Technology (CHT)
- Confederation of Indian Industry (CII)
- Department of Science and Technology (DST)

The R&D needs to reach to the stakeholder and for this collaboration with OTHER Groups and Industries is very important.

Thank You