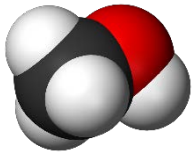


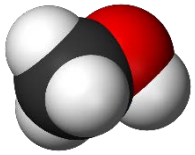
Effective catalysts for methanol synthesis: NPC-RT experience

Saeed Sahebdelfar | Head of Catalyst Research Group | NPC-R&T

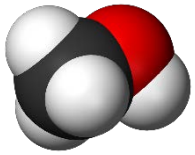
13th Iran Petrochemical Forum

April 22-23, 2017, Tehran, Iran

Presentation overview

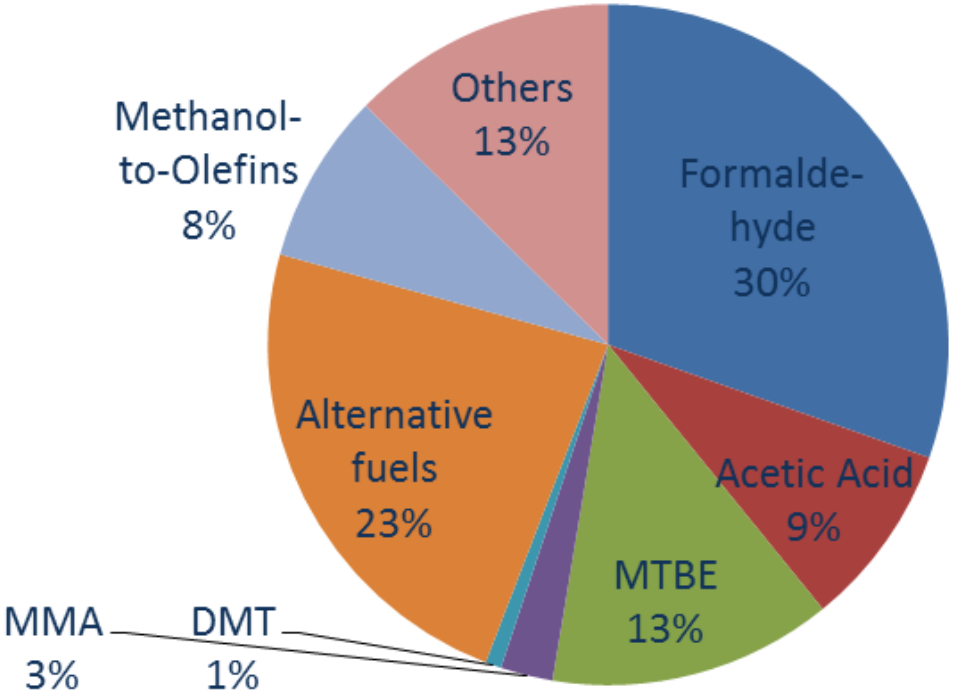


- Methanol as a basic chemical
- Methanol synthesis catalyst
- NPC-RT approach
- Characterization and performance results
- Some final remarks



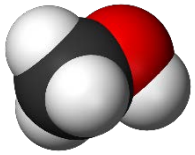
- **Methanol as a basic chemical**
- **Methanol synthesis catalyst**
- **NPC-RT approach**
- **Characterization and performance results**
- **Some final remarks**

Worldwide consumption of methanol



Source: http://www.methanol.org/methanol-basics/the-methanol-industry.aspx

Methanol synthesis reactions



- **Main methanol synthesis reaction:**

$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ $\quad \Delta H^\circ_{298} = -49.47$ kJ/mol

$\Delta G^\circ_{298} = +3.30$ kJ/mol

- **Water gas shift : (provides CO_2 for above reaction)**

$CO + H_2O \rightleftharpoons CO_2 + H_2$ $\quad \Delta H^\circ_{298} = -41.47$ kJ/mol

$\Delta G^\circ_{298} = -28.64$ kJ/mol

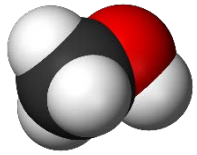
- Key reactions
- Rapid reactions

- **Conversion CO to methanol reaction:**

$CO + 2H_2 \rightleftharpoons CH_3OH$ $\quad \Delta H^\circ_{298} = -90.64$ kJ/mol

$\Delta G^\circ_{298} = -25.34$ kJ/mol

Slow reaction



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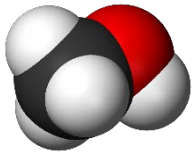
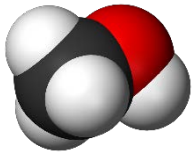
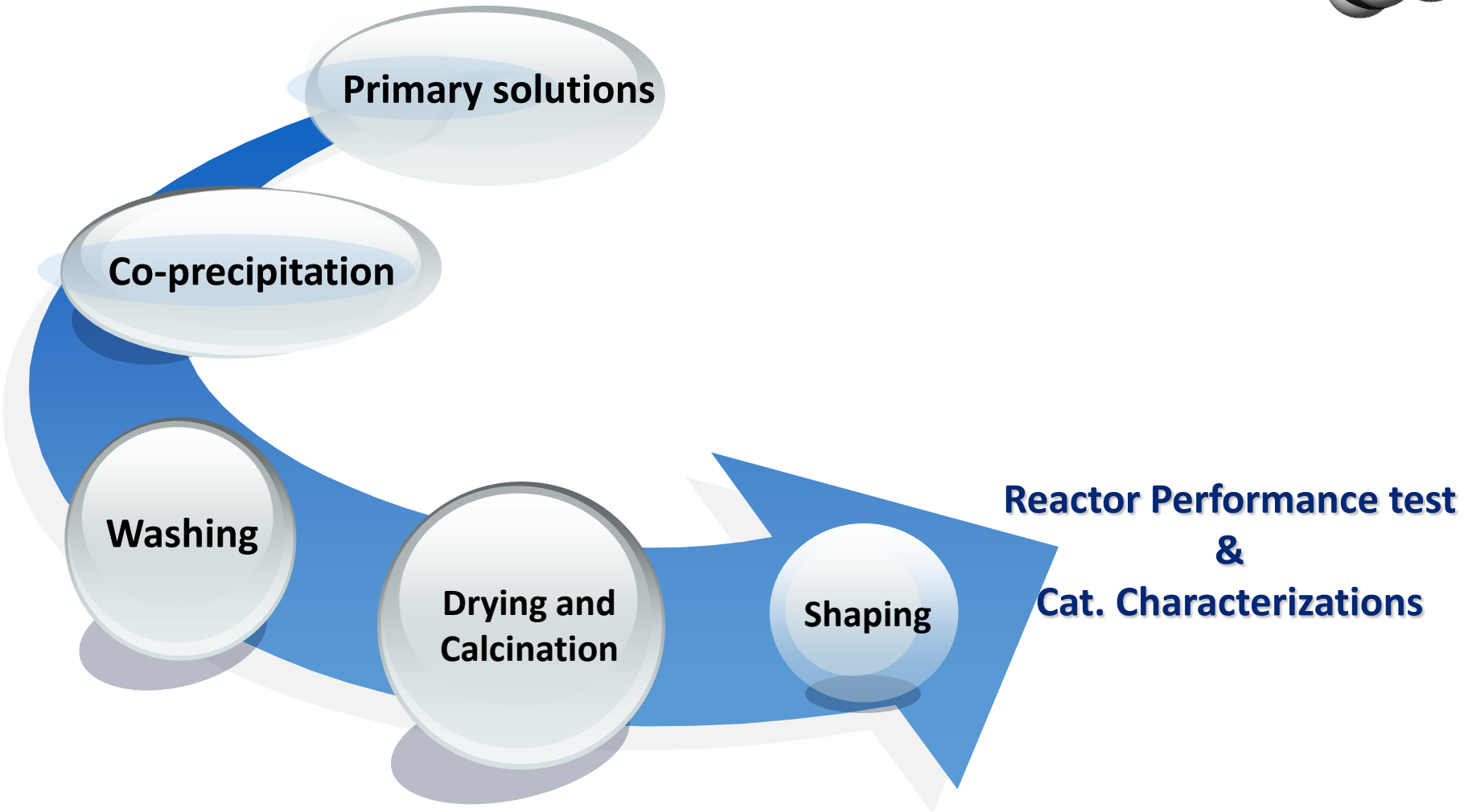
Global MeOH synthesis catalyst market

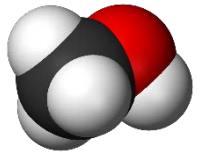


	Regions	Approx. Reactor Volume (m^3)
1	China	6800
2	Middle East and Africa (MEA)	4900
3	South America	3200
4	Asia Pacific and India	3100
5	Former Soviet Union (FSU)	2800
6	North America	2600
7	Europe (EU)	1600
	Approx. Total Market Size	~ 25000 m^3

$CuO/ZnO/Al_2O_3$ catalyst preparation outline







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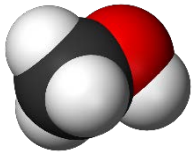
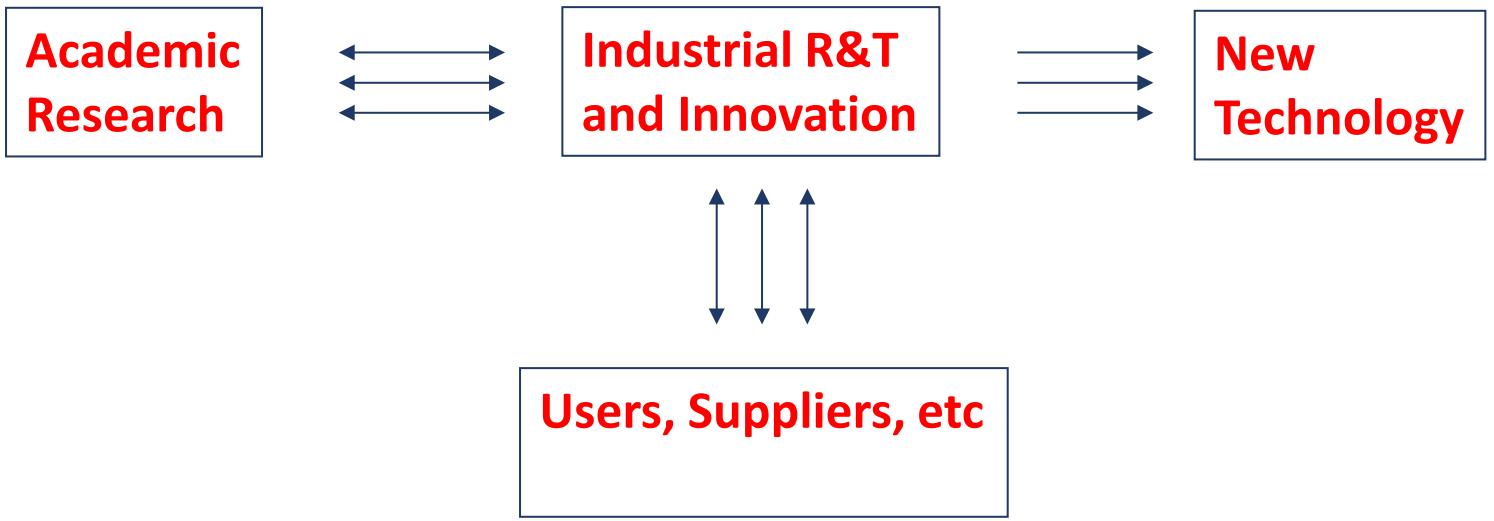
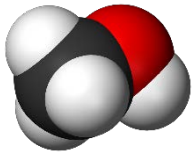
Industrial innovation process





J.R. Rostrup-Nielsen, in E.G. Deroune et al.(eds) Combinatorial Catalysis and High Throughput Catalyst Design and Testing, 337-371, 2000



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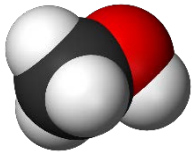
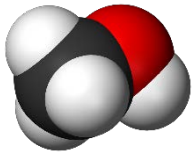
Industrial catalyst performance and key features



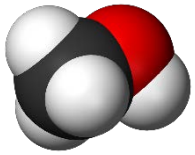
- High activity (High Cu surface area)
- High stability and resistance to deactivation (Stable Cu particle size and surface area)
- Low by-product creation
- Effective interaction between catalyst components
- High mechanical strength and slight shrinkage

Selected catalyst types



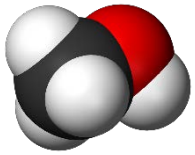
- NPC-RT Reference Method catalyst
  - (prepared by conventional method under optimized condition)
- NPC-RT Novel Method catalyst
  - (prepared base on a patented novel method)
- Two authentic and reliable commercial samples

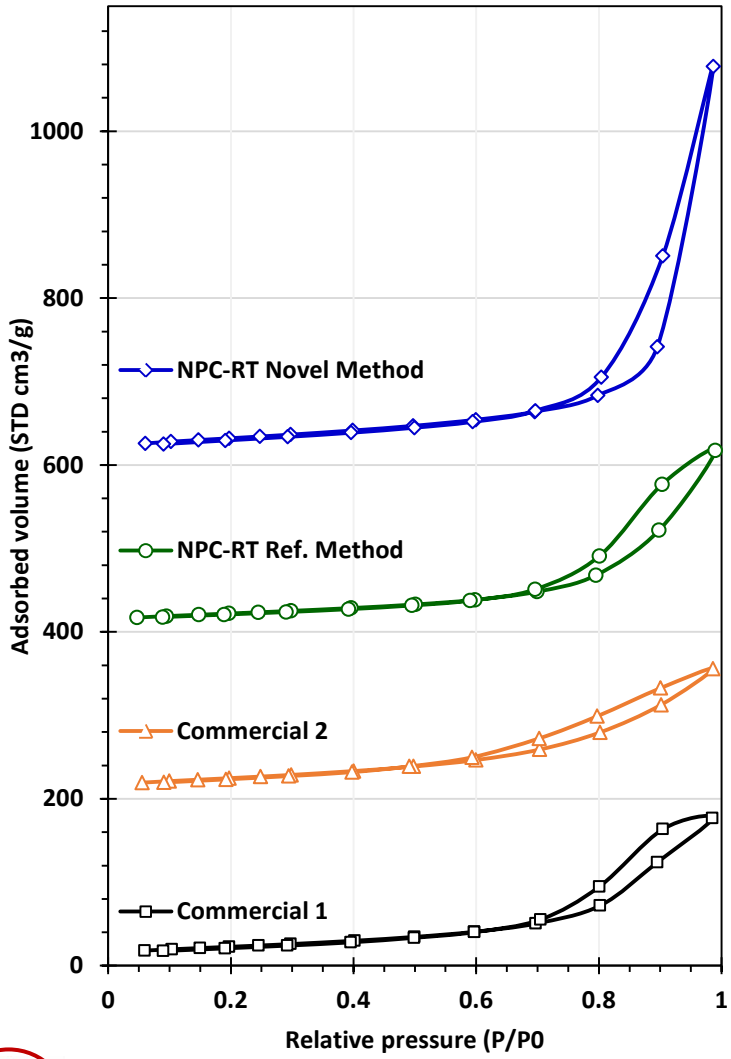
Catalyst characterization and evaluation



- Bulk properties (composition, phase structure)
- Particle properties (texture, mechanical properties)
- Surface properties (morphology, dispersion)
- Activity (fixed-bed reactor testing under relevant industrial condition and kinetic controlled condition)

N_2-physisorption isotherms



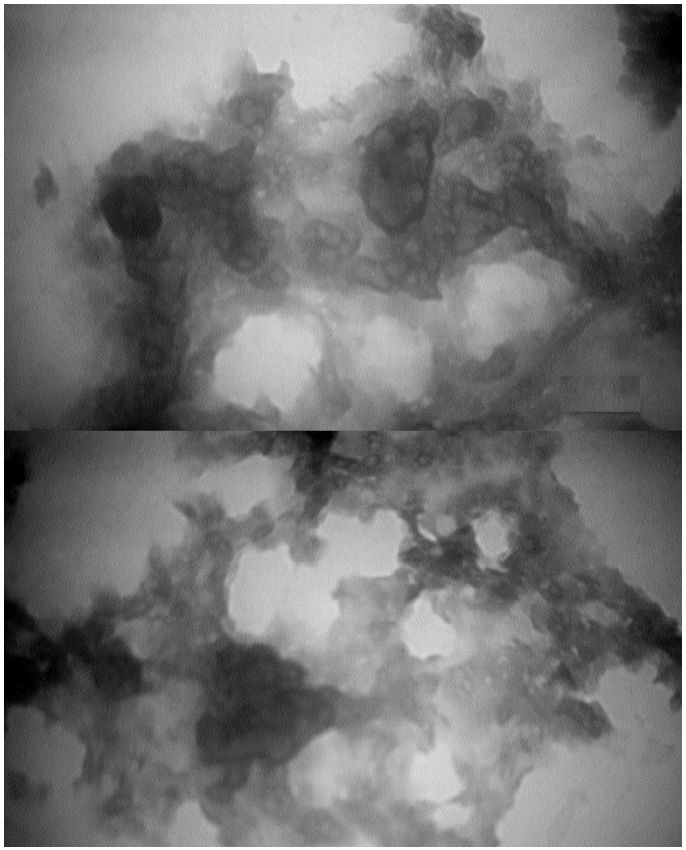


- Type IV isotherms
- Mesopores range (2 nm < pore diameter <50 nm)
- Relatively large cavities mesopores
- H1 type hysteresis
- Novel method catalyst have high adsorption volumes compared to that of reference catalyst being prepared by conventional method

For clearness, the isotherms for catalysts are vertically offset by 200, 400 and 600 cm^3g^{-1}, respectively.

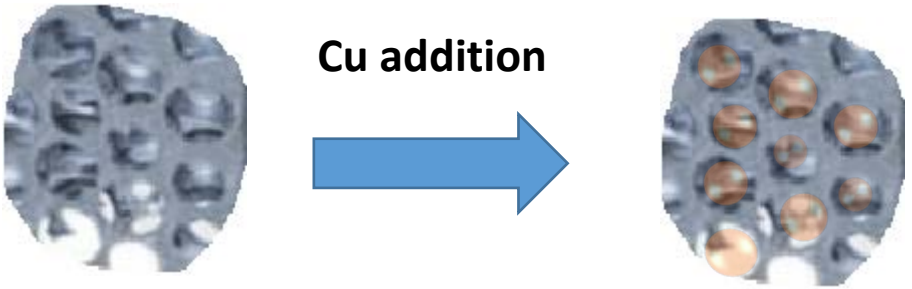
TEM of intermediate step in catalyst production

ZnAlO network



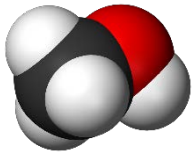
TEM image of nanoparticles of the dyadic Al-Zn intermediate network

- Nanoporous structure
- Hierarchically nanoporous frameworks of nanocrystalline Zn and Al oxides
- The Cu particles could be ensnared in the Al-Zn 3D network morphology.
- High CO_2/CO adsorption capacity, low diffusion limitation



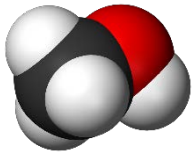
ZnAlO network

XRD analysis base on Scherrer equation



XRD analysis	Catalyst	CuO mean crystallite size (nm)	Used catalyst Cu mean crystallite (nm)	difference between CuO and Cu crystallite (nm)	Relative change in crystalite sizes (%)
	NPC-RT Ref. Method	6.1	11.8	5.6	47.9
	NPC-RT Novel Method	3.6	6.2	2.7	42.9
	Commercial 1	5.5	11.8	6.3	53.3
	Commercial 2	5.6	8.5	2.8	33.4

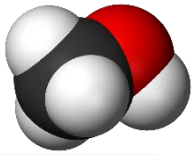
Nitrous oxide (N_2O) chemisorption
Measurement Cu specific surface area

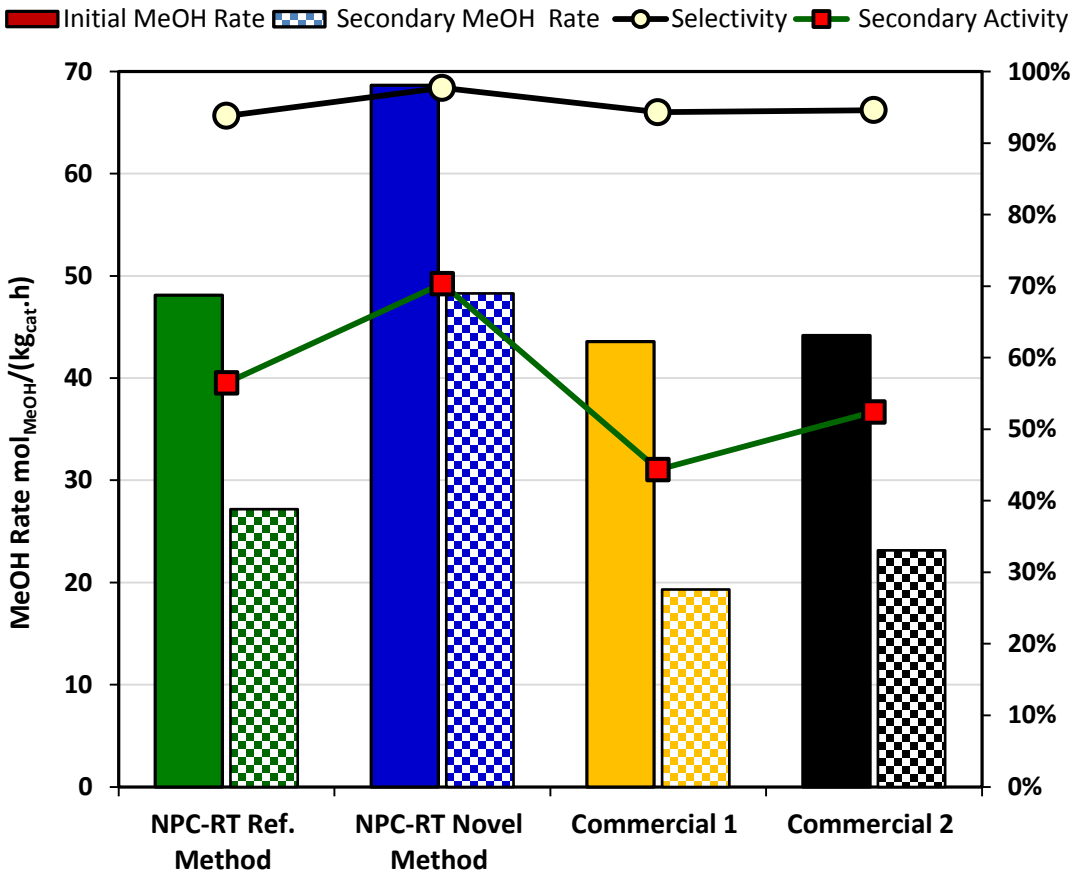


N_2O chemisorption	Catalyst	Metallic Cu specific surface area (m^2/g)	Metallic Cu dispersion (%)	$d_{Cu}(N_2O)$*
	NPC-RT Ref. Method	35.4	11.9	8.8
	NPC-RT Novel Method	55.4	18.5	5.6
	Commercial 1	29.1	9.7	11.2
	Commercial 2	28.9	9.7	12.2

*Fresh catalyst Cu crystallite size as estimated from copper specific surface with a spherical particle model

Initial and secondary methanol production rates, selectivity and secondary activity for catalysts



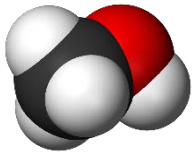


Reaction conditions:

- T = 230 °C
- P = 50 bar
- Space velocity = 17250 h^{-1}

- Synthesis gas feedstock ratio: $H_2/CO/CO_2$ = 80:12:8 (mol%)
- Max. (CO and CO_2) conversion of 40–45%.

Catalyst performance results

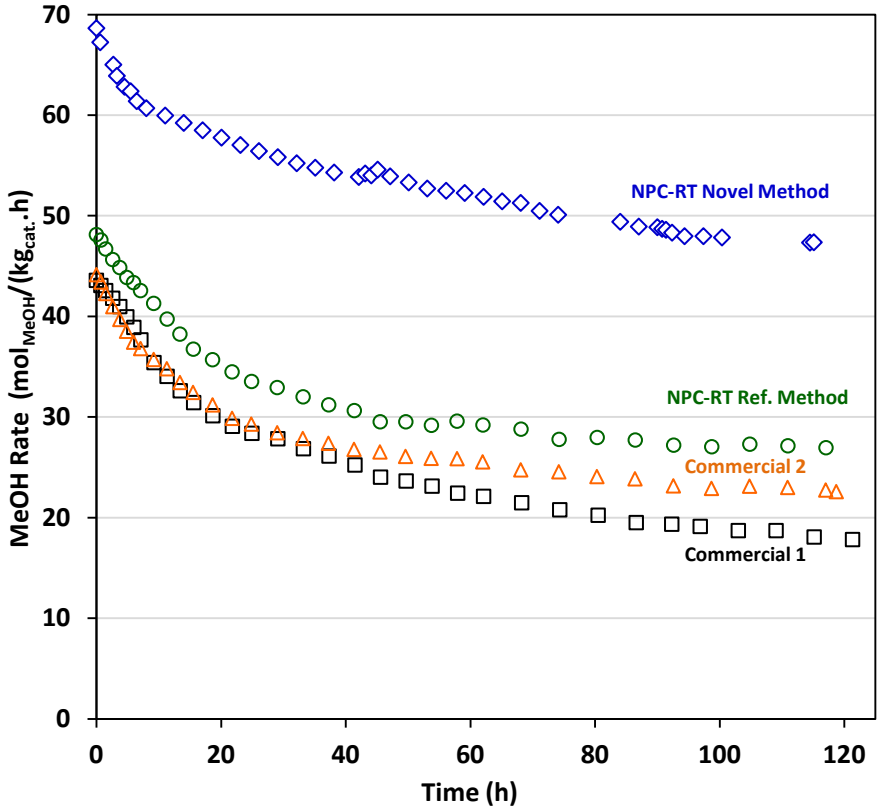


	Primary catalyst performance			Secondary catalyst performance		
	Primary MeOH rate (mol_{MeOH}/($h.kg_{cat}$))	MeOH reactor outlet (mol%)	MeOH selectivity (%)	Secondary MeOH rate (mol_{MeOH}/($h.kg_{cat}$))	MeOH reactor outlet (mol%)	Secondary activity (%)
NPC-RT Ref. Method	48.12	8.94	93.8	27.19	4.78	56.5
NPC-RT Novel Method	68.65	11.10	97.7	48.85	7.58	71.2
Commercial 1	43.56	8.01	94.3	19.33	3.29	44.4
Commercial 2	44.16	8.36	94.6	23.16	4.03	52.4

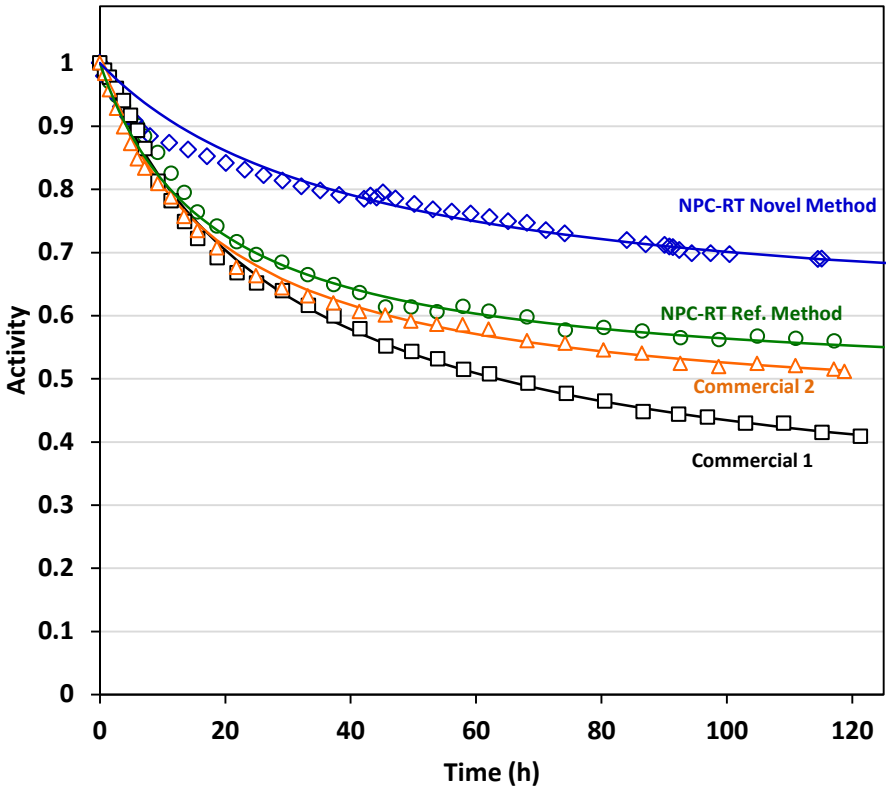
- Novel method catalyst is a very high performance catalyst

Activity and stability of catalysts versus time

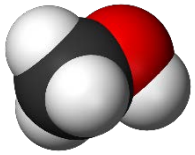
Methanol production rate versus time

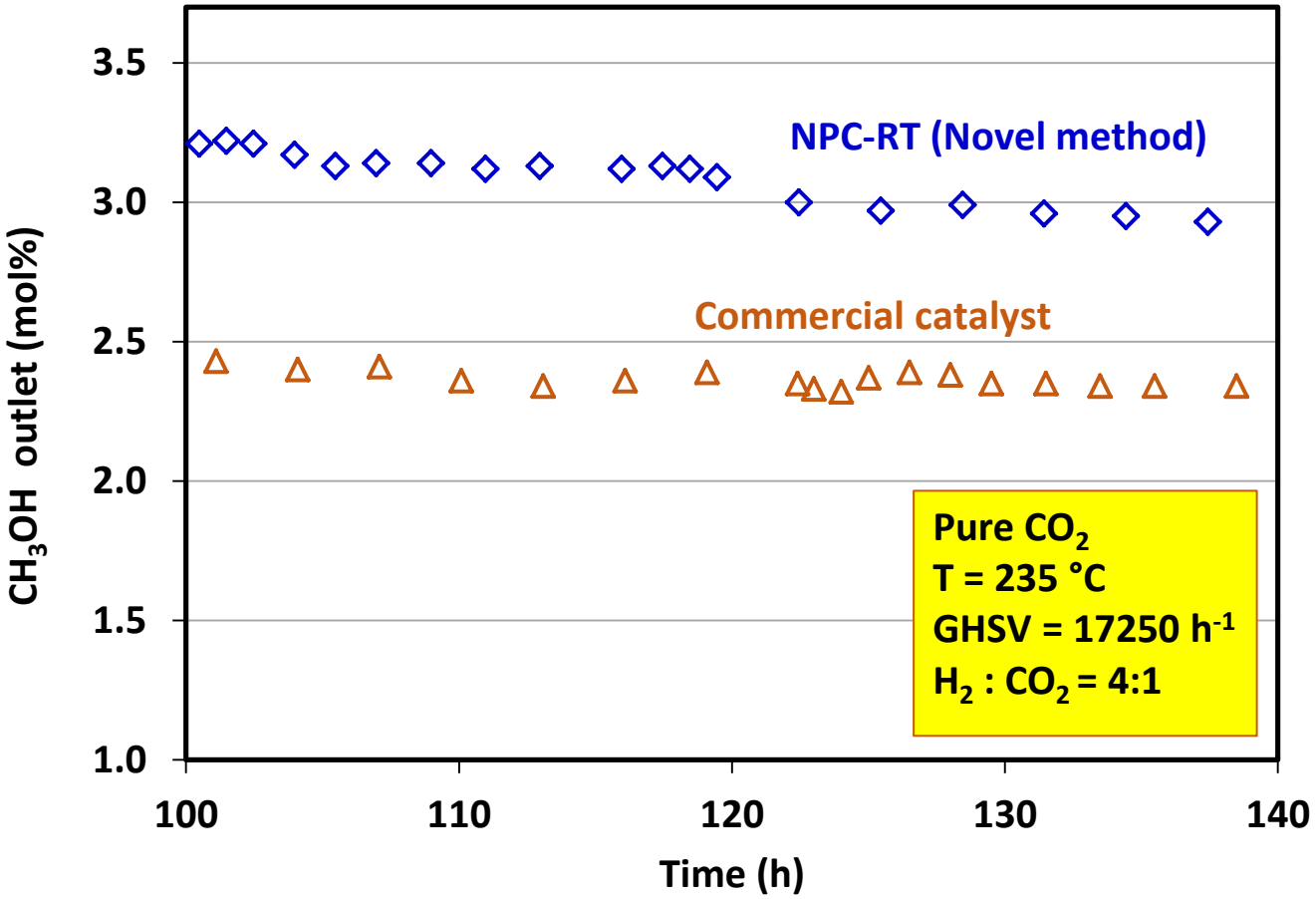


Normalized methanol synthesis activity over time for catalysts

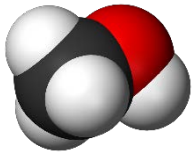


Performance of catalyst in MeOH synthesis from pure CO_2



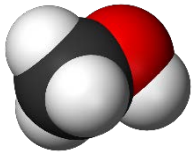


Some final remarks



Novel method catalyst have:

- **High surface area, pore volumes and pore size compared to competitors**
  - **Low diffusion limitation**
  - **Reduced by-product formation**
- **Highest methanol productivity**
  - **Increased plant throughput**
  - **Significant energy savings in synthesis loop**
- **High methanol selectivity**
  - **Increased carbon efficiency**
  - **Lower energy consumption in distillation section**
- **Most durable activity**
  - **Less catalyst replacements**
- **Good tolerance to high content CO_2 in feed or even pure CO_2 feedstock**
- **Feasible preparation method**
- **Agreement with a producer for commercial production (underway)**



Thank you for your attention

Any Question?