中国石油

Natural Gas Utilization for Chemicals production

CNPC

2021.4




CNPC is the largest natural gas producer and supplier in China. So far, natural gas is mostly used as clean energy. Natural gas to ammonia, natural gas to hydrogen, and natural gas to methanol are the main paths for its chemical utilization.

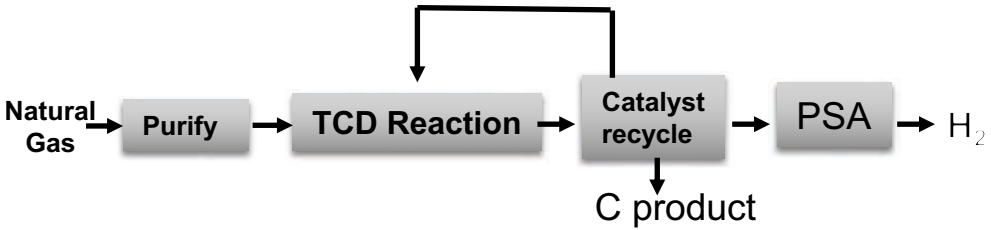
In addition to advancing natural gas exploration, high-efficiency purification of natural gas, and promoting the replacement of clean energy, CNPC attaches great importance to technical research in deep utilization of natural gas, such as H_2 production from methane decomposition, chemical looping for H_2 production, oxidative coupling to produce ethylene, and natural gas electrochemical utilization, etc.. Positive progress has been achieved in these areas, and some research works have entered industrial application stage.

PetroChina's Research and Development of Natural Gas Utilization Technology

- Natural gas catalytic decomposition to produce hydrogen and carbon materials
- Hydrogen Production via Chemical Looping Process
- Natural gas for power generation via fuel cell
- Direct Synthesis of Aromatics from Syngas
- Ethylene production via oxidative coupling of methane from natural gas
- Chemicals production from syngas via Fisher-Tropsch

Natural gas catalytic decomposition for H_2 and carbon material production (TCD Technology)

Our research of catalysts and processes for H_2 and carbon nanomaterials production focuses on direct catalytic decomposition of natural gas. We developed a metal catalyst with special structure of high strength and wear-resistant. The total carbon conversion rate of natural gas is ≥50.0%, and 95.0% of the carbon material is multi-walled nanotube material.



TCD Process

Cost Analysis for different H_2 production routes

	Conventional natural gas to Hydrogen Route	TCD Route
Raw material	9103	12741
Additives	100	120
Energy cost	2982	3100
Worker Salaries	149	149
Equipments	1109	831
Total cost	13443	16941
By-product value	0	-15000
Overall cost	13443	1941
Cost per m^3 H_2, RMB/m^3	1.21	0.17

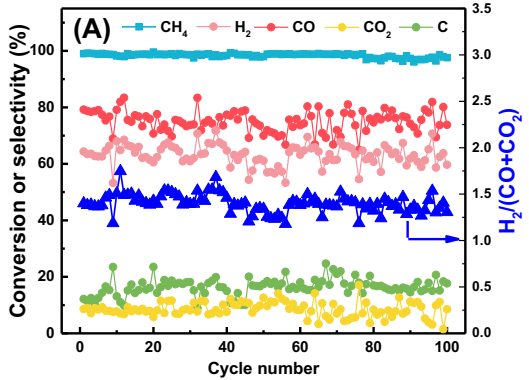
Hydrogen Production via Chemical Looping Process

Chemical looping process, whereby a reaction can be broken down into multiple sub-reactions that take place in isolated steps or spaces. The process system can integrate the conversion of the fuel and separation of the production in one step.

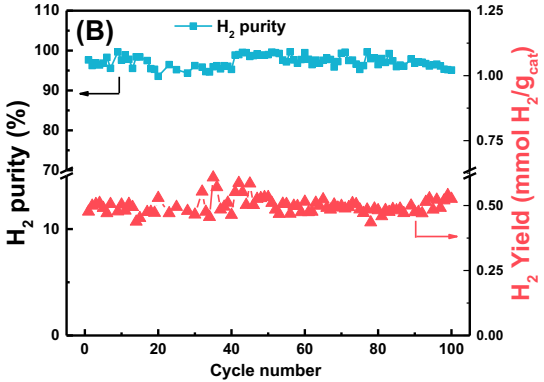
Reducer step: $CH_4+MeO_m \rightarrow MeO_n+CO+2H_2$, Methane conversion is above 99%.

Oxidizer step: $MeO_n+H_2O \rightarrow H_2+MeO_m$, Hydrogen purity is above 95%.

Methane conversion and syngas selectivity remain stable for 100 cycles test.



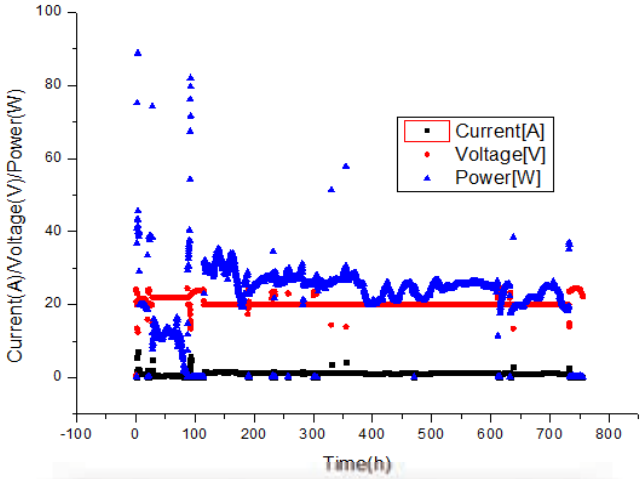
Reducer step test



Oxidizer step test

Natural gas for power generation via fuel cell

We have achieved power generation from natural gas by solid oxides self-heating process. Single cell power density has reached 8 W , stack power density 89W , power generation efficiency ≥40%。



Direct Synthesis of Aromatics from Syngas

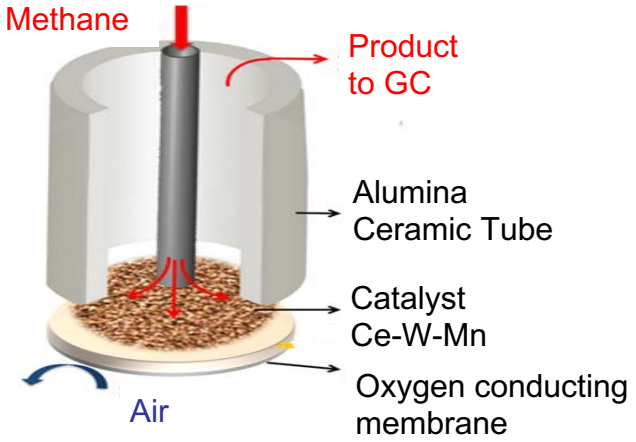
A dual-functional catalyst has been developed for direct synthesis of aromatics from syngas with good stability, high activity and high selectivity.We have completed the research on small-scale process technology and realized the one-step synthesis of mesitylene from syngas. Results show that CO conversion rate reaches 90% at 370℃, and aromatics selectivity is 60%, among which the selectivity of mesitylene in aromatics reaches 40%.

Main targets achieved

	item	Currently reaching index
Process conditions	reaction temperature/℃	370
	reaction pressure/MPa	4. 0
Technical and economic indicators	Single pass conversion of CO/%	90
	Aromatics selectivity/%	≥60
	Mesitylene selectivity/%	40

Ethylene production via oxidative coupling of methane from nature gas

An Oxidative Coupling of Methane-Solid Oxide Fuel Cell (OCM-SOFC) integrated reactor has been developed. Oxygen from air dissociated into ion on the cathode of SOFC, transffered into the anode via oxygen conducting membrane, and accelerated methane conversion. In our reaction system, there was no direct mix of methane and oxygen molecule, so no danger of explosion; moreover, compared with traditional OCM, we could achieve better ethylene yield. Recently, we are carrying out the scale-up research.



OCM-SOFC integrated reactor

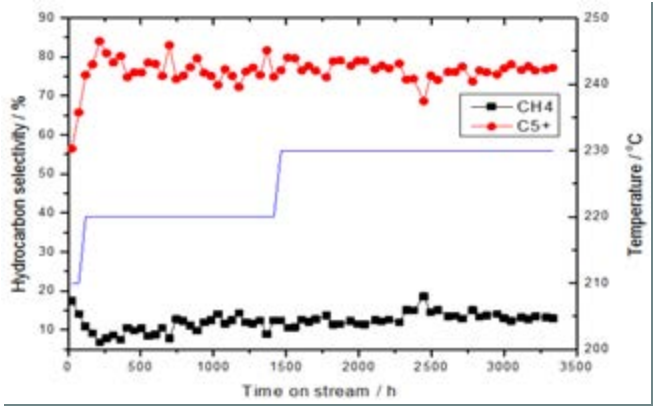
Results from OCM-SOFC integrated reactor and the conventional OCM

	Petrochina	Conventional OCM
Methane conversion/%	39	25
C2+ Selectivity/wt%	57.6	57
Ethylene：Ethane（mol）	5:1	1:2

Chemicals production from syngas via Fisher-Tropsch

High value-added chemicals, including synthetic wax, lubricating oil and drilling fluid could be produced from nature gas based syngas via Fischer-Tropsch. The products are Free of sulfur, aromatics and heavy metals.

Based on the Fischer-Tropsch catalyst developed by Petrochina: Selectivity of C12-C25>35wt%, C25+>45wt%. Synthetic drilling fluid base oil : Viscosity (mm^2/s, 40℃) ≤ 2.8 , Flash point > 90℃ , Pour point < -20℃ , Sulphur content < 0.5ppm.



Long-time lab test for catalysts stability evaluation

Base oil sample

Future Perspectives

Natural gas will play a more crucial role in future energy and chemicals field, especially for low-carbon development. More industrial applications are expected to utilize natural gas as important chemical raw material.

The technical difficulties encountered in traditional catalytic process can be solved by unconventional means such as electro-catalysis. If green power technology applied in large-scale in the future, electro-conversion of methane/CO_2 and other technical applications will provide technical support for low-carbon development. Natural gas utilization will develop toward green, low-carbon, and atomic economy. CNPC will continue to collaborate with global partners to promote research and development for in-depth utilization of natural gas, practice the concept of green and low-carbon development, and make greater contributions to achieving carbon neutrality and achieving net zero emissions at an earlier date.

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