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Production of GHG free hydrogen from methane: significance of porosity of NiO/SiO_2 nanocatalysts

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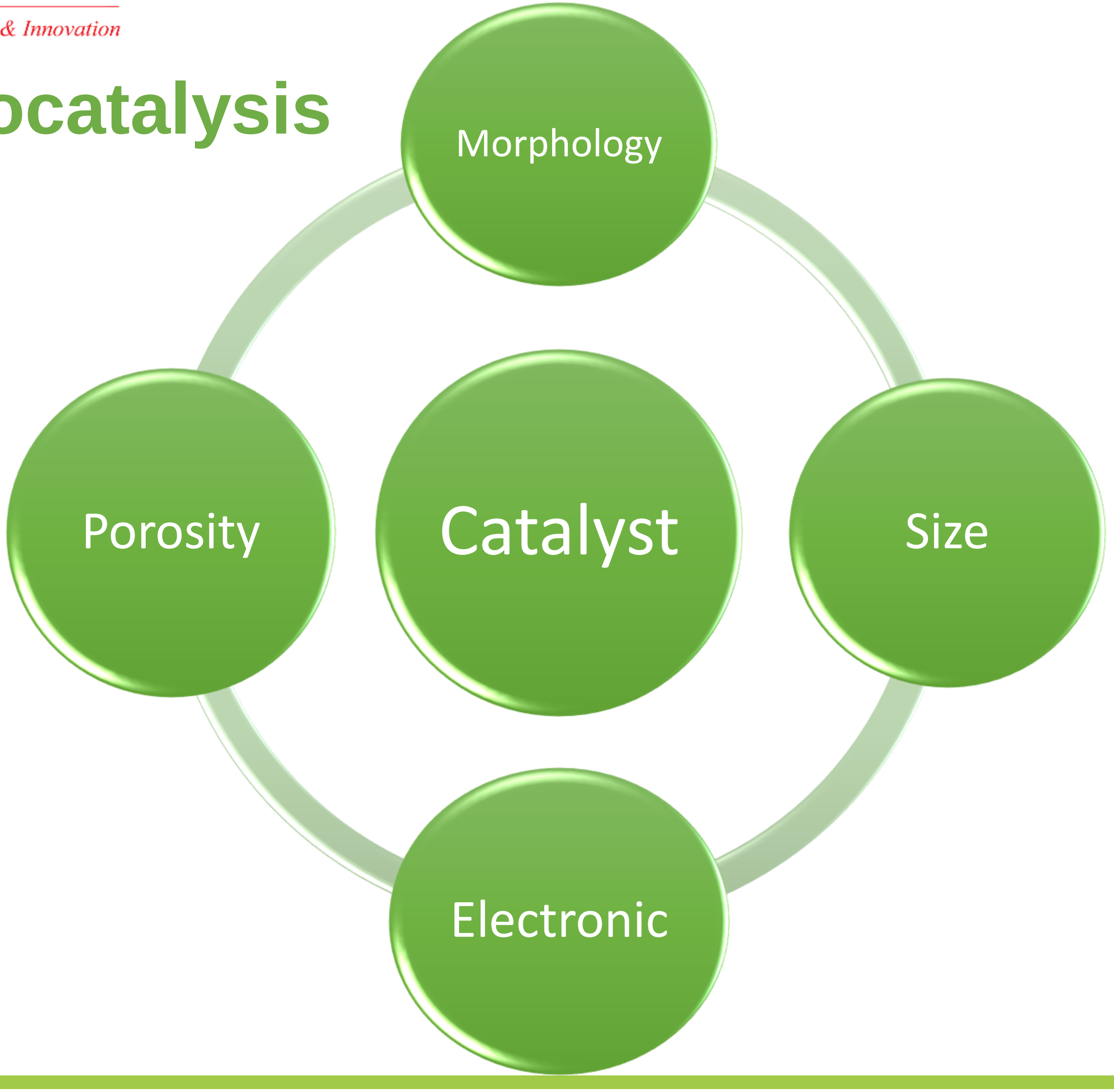
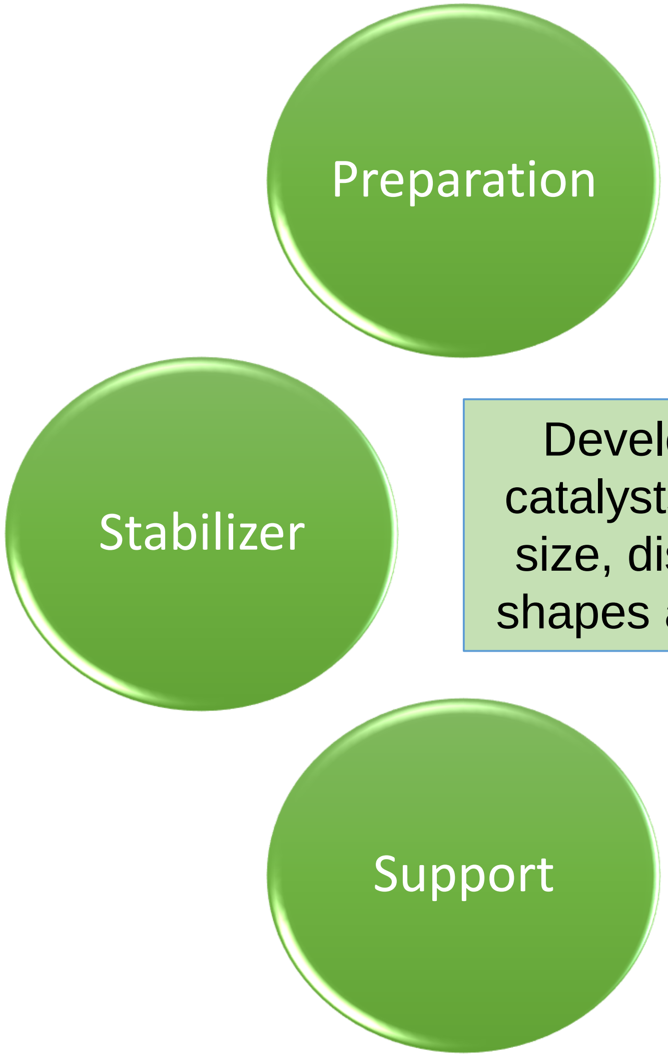
Nanoscience and nanotechnology

- Exclusive properties compared to their bulk counterparts
- Finite size effect
- Surface effect
- Macroscopic quantum tunneling effect
- Optical
- Electronic
- Magnetic

- Catalysis
- Fuel cells
- Gas sensors
- Photo-electronic devices
- Energy storage devices
- Super-capacitors
- Lithium ion batteries

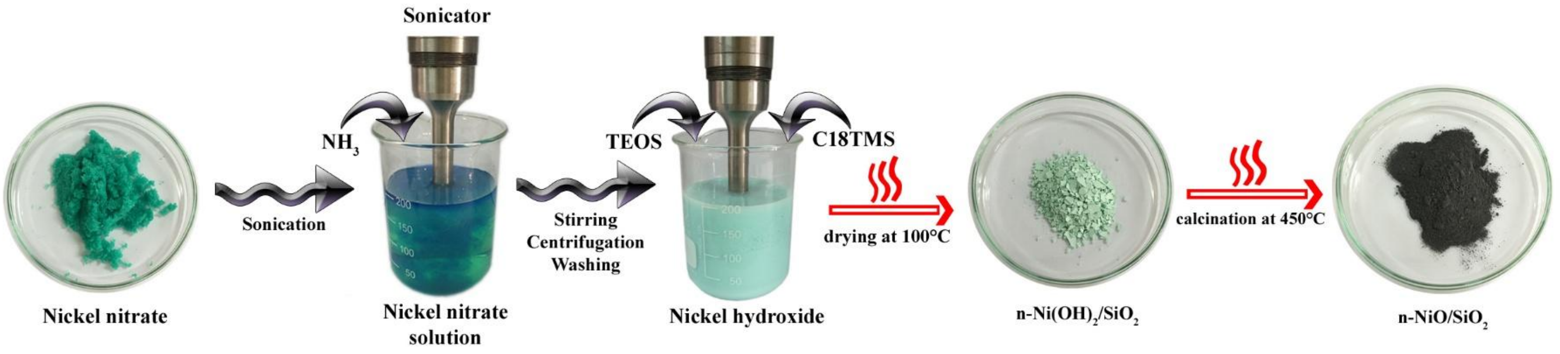
Nanocatalysis





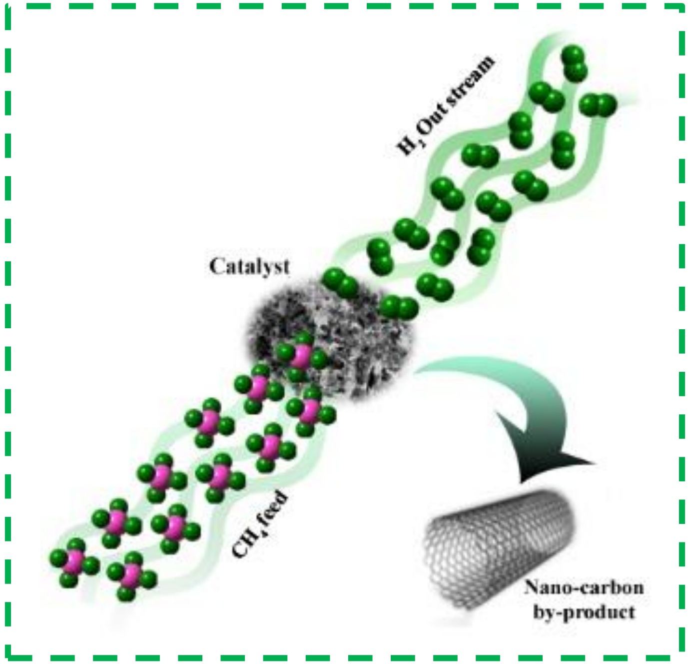
Development of catalysts with lower size, distinguished shapes and porosity

Preparation of *n*-NiO/SiO_2 catalyst



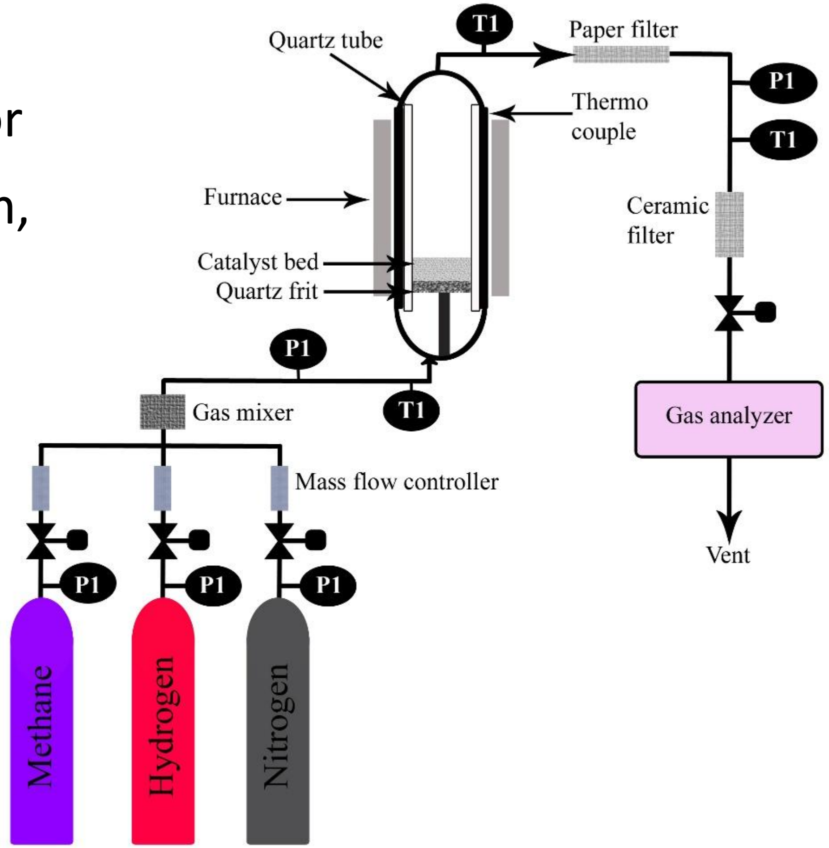
Catalyst	$Ni(NO_3)_2.6H_2O$ (gm)	TEOS (mL)	C18TMS (mL)
S1	17.45	0.6	0.6
S2	17.45	1.2	0
S3	17.45	0	1.2
S4	17.45	0.9	0.3
S5	17.45	0.3	0.9

Thermocatalytic decomposition of methane



- Fixed catalyst bed reactor
- Inner diameter = 3.03 cm,
- Wall thickness = 0.87 cm
- Height = 120 cm

- ***0.5 g of catalyst***
- ***Reduction at 550 °C***
- ***99.995% methane***
- ***TCD at 625 °C***



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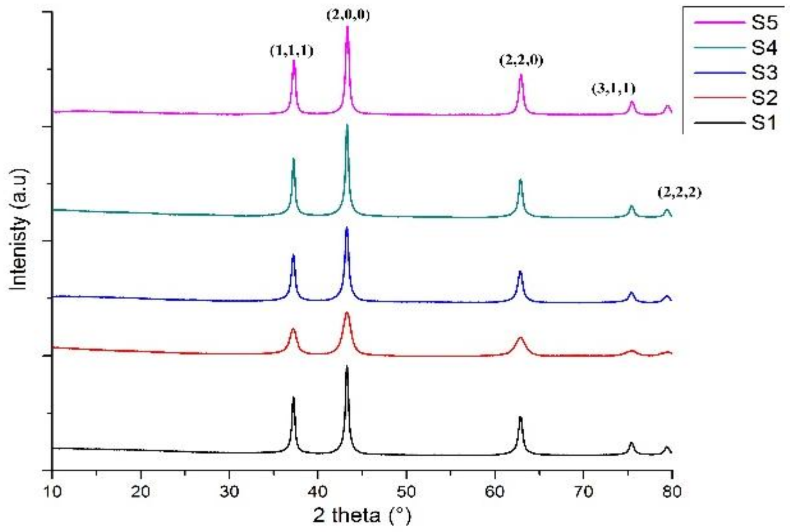
XRD



- Good agreement with JCPDS No.: 01-073-1523 for NiO phase
- S2 - 1.2 mL of TEOS - lower intensity - lower structural ordering - poor catalytic stability
- 1.2 mL of C18TMS and mixture of TEOS and C18TMS - better crystal order - catalytic performance

Sample	2θ (°)	Ni (111) (nm)	Ni (200) (nm)	Ni (220) (nm)	Avg. crystal size (nm)
S1	37.22, 43.26, 62.81	31.13	31.74	34.57	32.48
S2	37.21, 43.23, 62.69	38.04	31.80	13.57	27.80
S3	37.22, 43.26, 62.84	26.34	24.93	23.77	25.01
S4	37.23, 43.27, 62.83	34.25	31.74	38.03	34.67
S5	37.30, 43.33, 62.91	24.46	23.28	25.36	24.37

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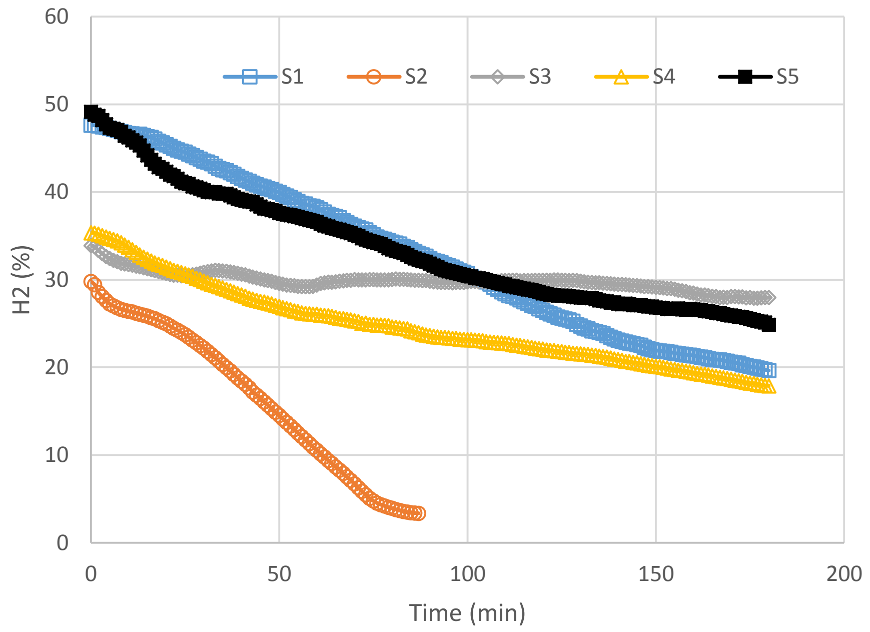
Nitrogen adsorption–desorption measurements

Catalyst	Single point SA[a] (m^2/g)	BET SA (m^2/g)	Micropore area[b] (%)	Mesopore + external area[c] (%)	Micropore volume[d] (cm^3/g)	Mesoporous volume (cm^3/g)	Total pore volume[e] (cm^3/g)	BET pore size (nm)	Mean particle size (nm)
S1	81.74	83.26	16.1	83.9	0.0059	0.1444	0.1503	8.182	36.02
S2	115.76	117.90	8.1	91.9	0.0051	0.1804	0.1855	7.072	25.44
S3	70.19	71.84	11.1	88.9	0.0066	0.1747	0.1813	9.273	41.75
S4	84.76	86.92	13.7	86.3	0.0065	0.1538	0.1603	7.400	34.51
S5	50.29	51.51	26.8	73.2	0.0079	0.1192	0.1271	6.702	58.92

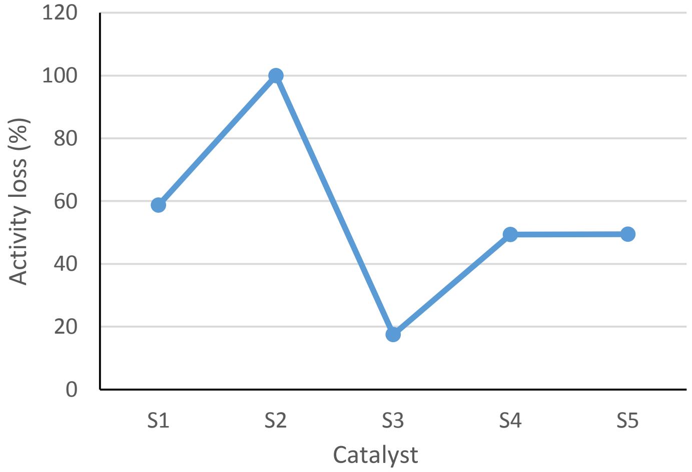
- Addition of C18TMS porogen increase microporous area
- 0.3 mL of TEOS and 0.9 mL of C18TMS - 26.8% of microporous area
- 1.2 mL of TEOS shown lowest microporous area (8.1%)

Thermocatalytic methane decomposition

- *n*-NiO/SiO_2 catalyst prepared by co-precipitation cum modified Stöber method rapidly deactivate above 675 °C
- S1 (0.6 mL of C18TMS and 0.6 mL of TEOS) exhibited stable performance with a higher hydrogen production
- S3 (0 mL of TEOS and 1.2 mL of C18TMS) executed lowest activity loss of 17.46%



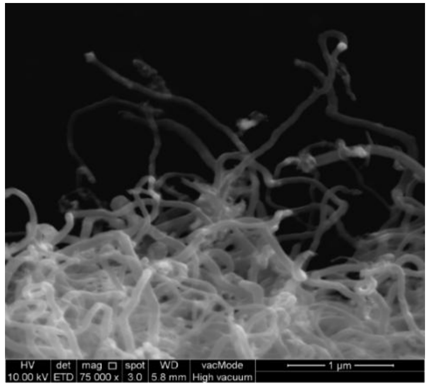
C18TMS produces higher amount of microporous area – higher stability



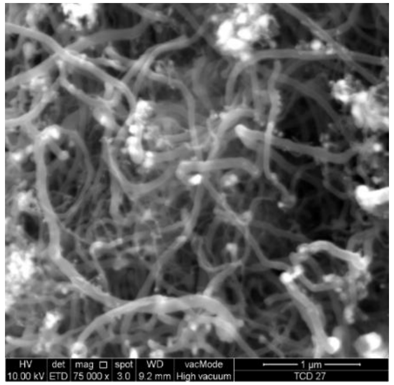
Ashik, U. P. M., & Daud, W. M. A. W. (2015). Nano-nickel catalyst reinforced with silicate for methane decomposition to produce hydrogen and nanocarbon: synthesis by co-precipitation cum modified Stober method. *RSC Advances*, *5*, 46735-46748. doi:10.1039/C5RA07098H

Thermocatalytic methane decomposition

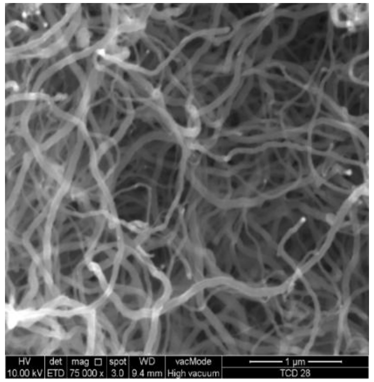
- Tip-growth mechanism of nano-carbon formation
- The crystallite size of S1, S2 and S3 calculated from XRD patterns were 26.1, 33.63 and 22.86 nm, respectively.
- The average diameter of nano-carbon measured with ImagJ software were 24.74±3.1 nm, 27.94±2.8 nm and 36.84±4.1 nm
- Average diameter of nano-carbon is decreasing as increasing the quantity of C18TMS



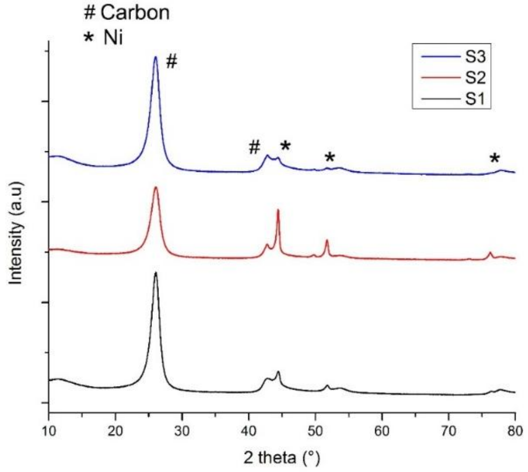
S1



S2



S3



Conclusion

- The particle size, porosity and catalytic activity management was efficiently governed by the systematic variance in the ratio of C18TMS porogen to TEOS silica precursor
- Microporous characteristics was increased from 10.7% to 26.8% by increasing the quantity of C18TMS compared to TEOS in preparation mixture
- Absence of C18TMS in the preparation mixture resulted in the lower crystal structure order and hence lower catalytic stability
- Maximum catalytic stability for methane decomposition was observed with catalyst prepared with 1.2 mL of C18TMS and 0 mL of TEOS
- Catalyst prepared with 0 mL of C18TMS and 1.2 mL of TEOS exhibited lowest catalytic stability

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