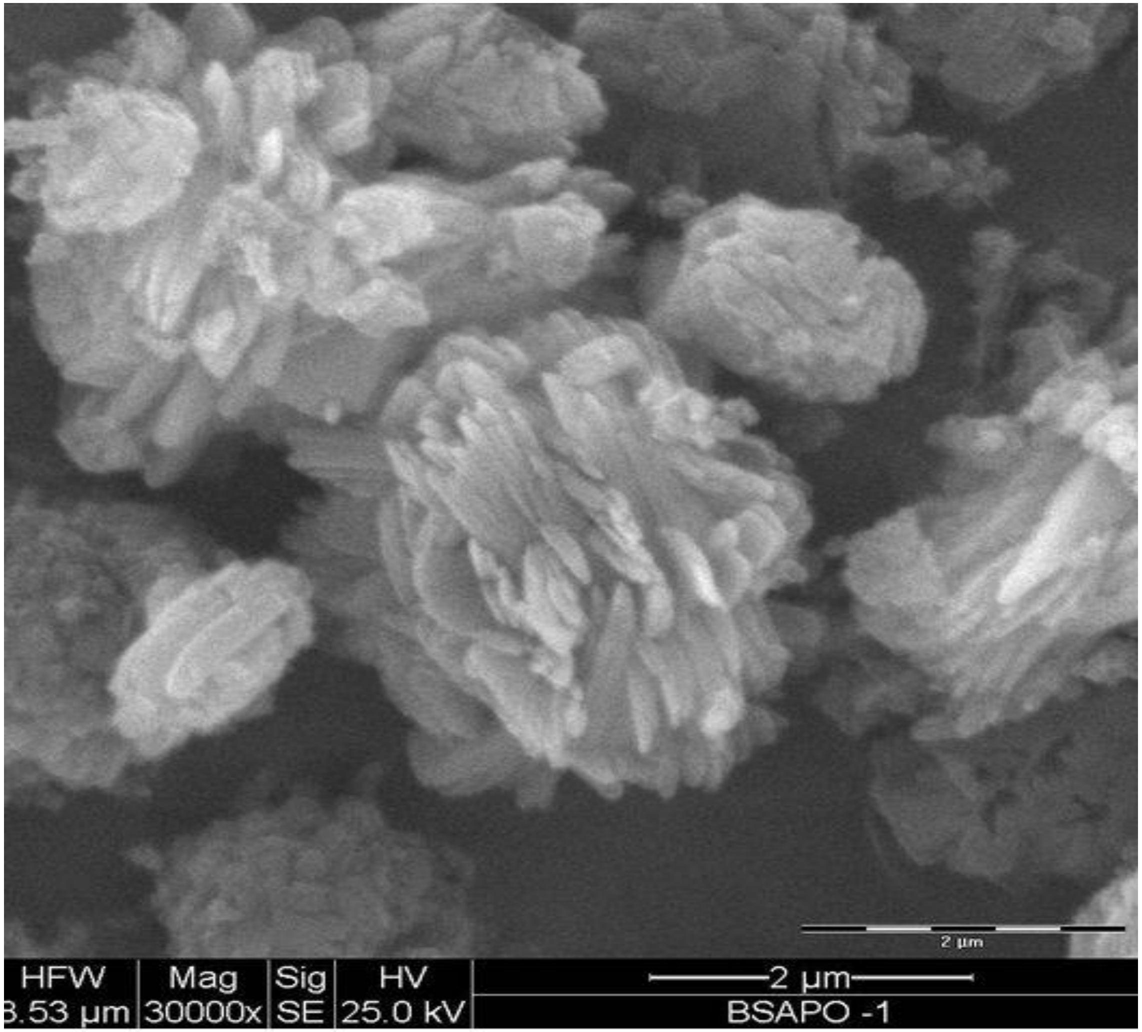
Ben-Gurion University of the Negev

Chemical Engineering Department

Blechner Center for Applied Catalysis and Process Development

Slides for 2011 report

Zeolite SAPO-11 with crystal size of 200-250 nm was synthesized in Blechner Center



Densified MgO-II catalyst displayed three times higher rate of high alcohols production from ethanol

Catalyst*)	MgO-I MgO aerogel	MgO-II (MgO aerogel;double chemical densification)
Ethanol conversion rate, mmol/g cat.*h	32	90
TOF, mmol/mmol B*h	19	19
High alcohols production rates, mmol/g cat.h: 1-butanol 1-hexanol	 6.4 0.7	 20.7 2.7

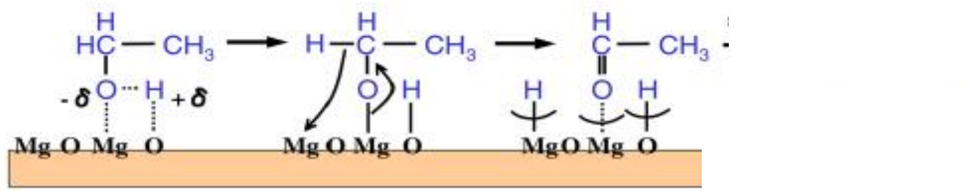
*Pretreatment temperature 650°C

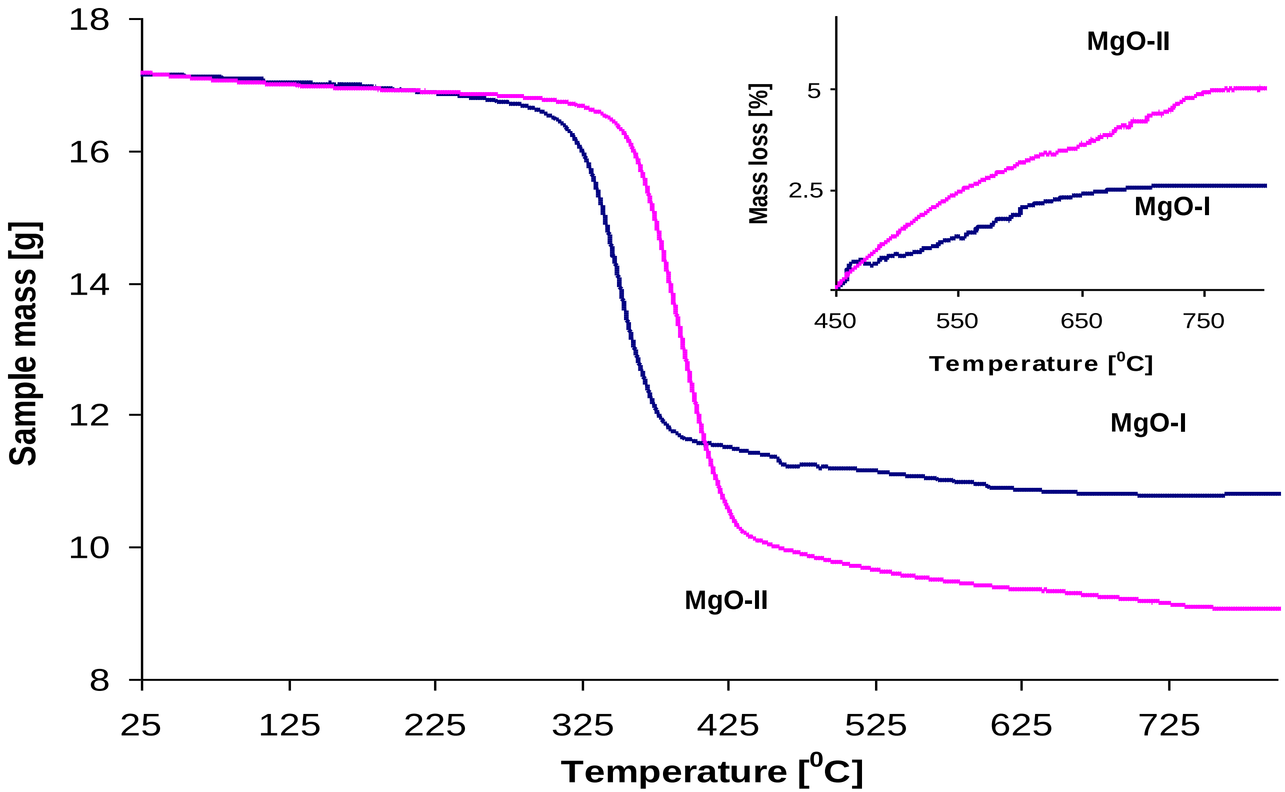
$$\text{Reaction rate} = \frac{\text{WHSV*X}}{100 * Mw_a} \quad [\frac{\text{mmol}}{\text{g}_{\text{cat}} h}] \qquad \text{TOF} = \frac{\text{Reaction rate}}{\text{B}} \quad [\frac{\text{mmol}}{\text{mmol}_{\text{site}} h}]$$

*B- concentration of basic sites per gram catalyst.

The reaction rate and TOF were calculated for 10-20% conversion of ethanol at 450°C:
MgO-I: WHSV = 5 h^{-1}; MgO-II: WHSV = 20 h^{-1}

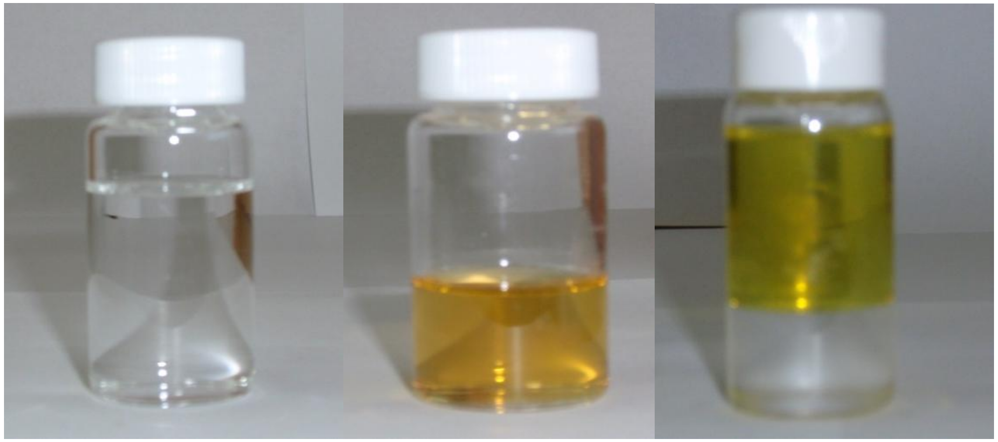
The surface acid sites (Mg-OH) are significantly more thermally stable in chemically densified MgO-aerogel





At high conversions MgO-II material catalyzes EtOH condensation to higher hydrocarbons and their significant deoxygenation

- MgO-I at 400-500°C did not display significant condensation / dehydration activity toward ethanol yielding one liquid phase high alcohols.
- Densified MgO-II aerogel at of 500-530°C yielded liquid product consisted of two fractions.



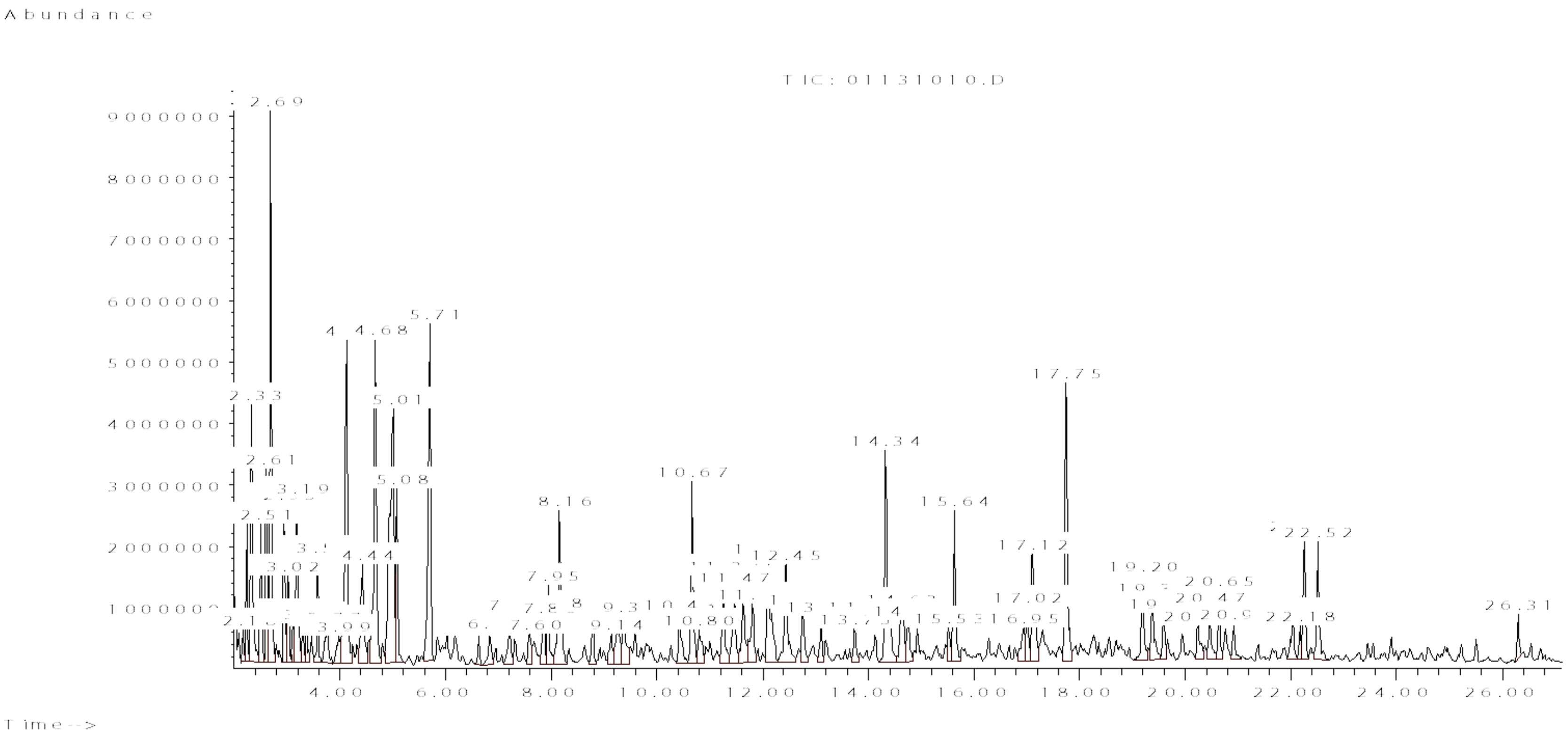
Starting EtOH	Product with MgO-I	Product with MgO-II

1. Organic phase (50%) consisted of oxygenates (alcohols, aldehydes, ketones) dissolved in hydrocarbons containing paraffins, olefins and light aromatics.

2. Aqueous phase (25%) containing water and dissolved lower oxygenates.

"Bio-fuel" components

The biofuel phase consists of more than 100 different molecules. The main components
Oxygenates – alcohols, aldehydes, ketones
Hydrocarbons – paraffins, olefins, aromatics
were identified by GC-FID and GCMS.



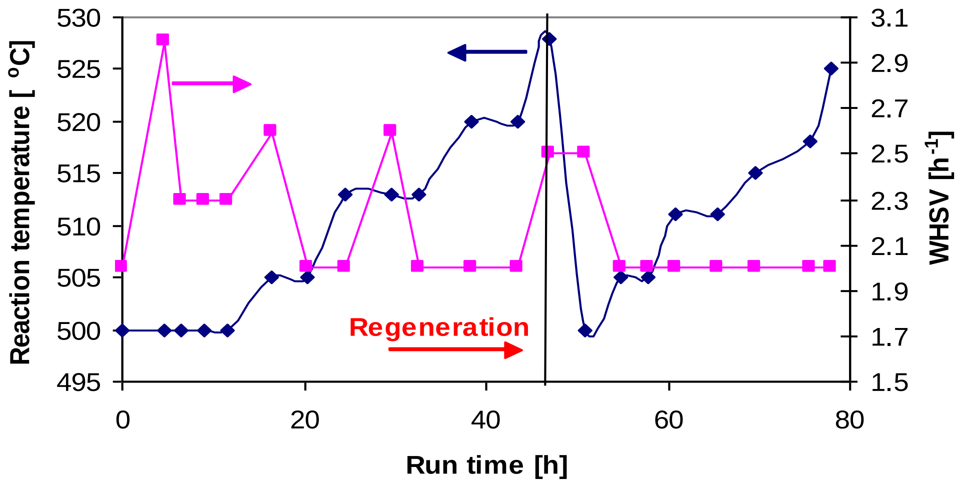
“Bio-fuel” components

Retention time[min]	Componen t name	Retention time[min]	Component name
1.95	2-Octanol	7.86	Propylbenzene
2.09	2-Hepten	7.95	2-Ethyl-Hexanal
2.17	Cyclohepten	8.17	1-ethyl,3-methyl Benzene
2.32	2-Methyl,1-Butanol	8.64	4-Octanone
2.51	4-Methyl,1,4 Hexadiene	8.79	1-ethyl,2-methyl Benzene
2.61	2-Ethyl-Butanal	9.14	3-Octanone
2.69	Toluene	9.27	1,2,3-trimethyl-Benzene
2.94	3-Hexanone	9.59	2-Ethyl-Hexenal
3.11	3-Hexanol	9.81	5-Decene
3.31	2-Octene	10.26	1,2,4-trimethyl-Benzene
3.58	2-Ethyl,2-Butenal	10.43	Cyclopropyl-Benzene
3.77	1,4 Dimethyl-1-cyclohexene	10.67	2-Methyl,1-Hexanol
4.14	2-Ethyl-Butanol	10.8	Benzyl alcohol
4.56	3-Hexen-1-ol	11.27	1,3 diethyl Benzene
4.69	Ethylbenzene	11.47	Butyl-Benzene
5.01	Formic acid. hexyl ester	11.64	2-methyl- Phenol
5.71	Xylene	12.77	2-Nonanone
5.95	Nonene	14.33	2-ethyl Phenol
6.03	2-Heptanol	15.64	2-ethyl,5-methyl-Phenol
6.96	3-Methyl,4-Heptanone	19.2	Thymol

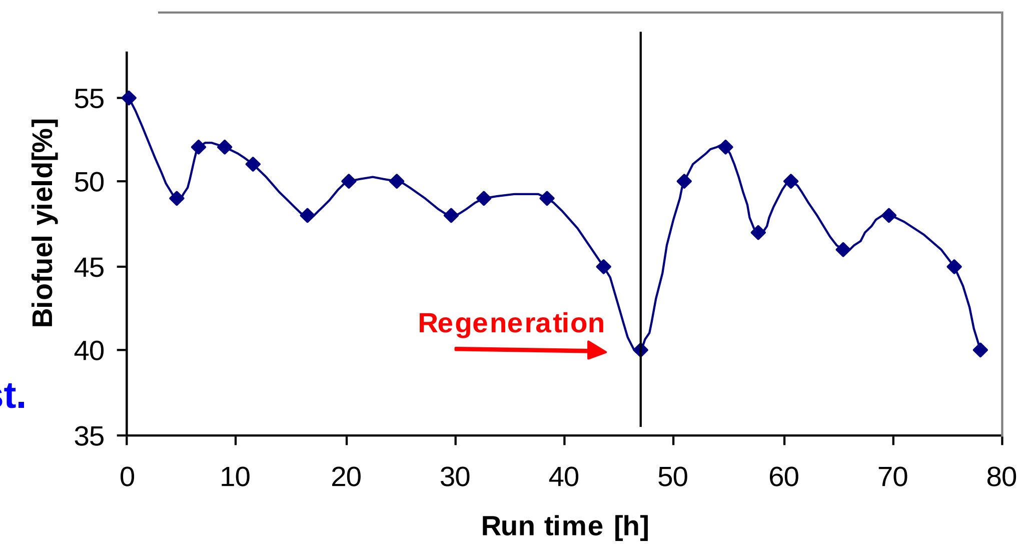
“Bio-fuel” properties

		Biofuel produced over MgC -II	Israel gasoline standard
Fuel property	Units		
Density	Kg/m^3	**830**	**720-775**
Distillation characteristic			
Initial boiling point	°C	56	
10 vol%	°C	70	
20 vol%	°C	**75**	**Max 70**
30 vol%	°C	78	
40 vol%	°C	82	
50 vol%	°C	**84**	**Max 100**
60 vol%	°C	93	
70 vol%	°C	116	
80 vol%	°C	**132**	**Max150**
90 vol%	°C	167	
95 vol%	°C	205	
Final boiling point	°C	**244**	**Max 210**

50% "Bio-fuel" yield was obtained at high EtOH conversions in two continuous runs with MgO-II catalyst

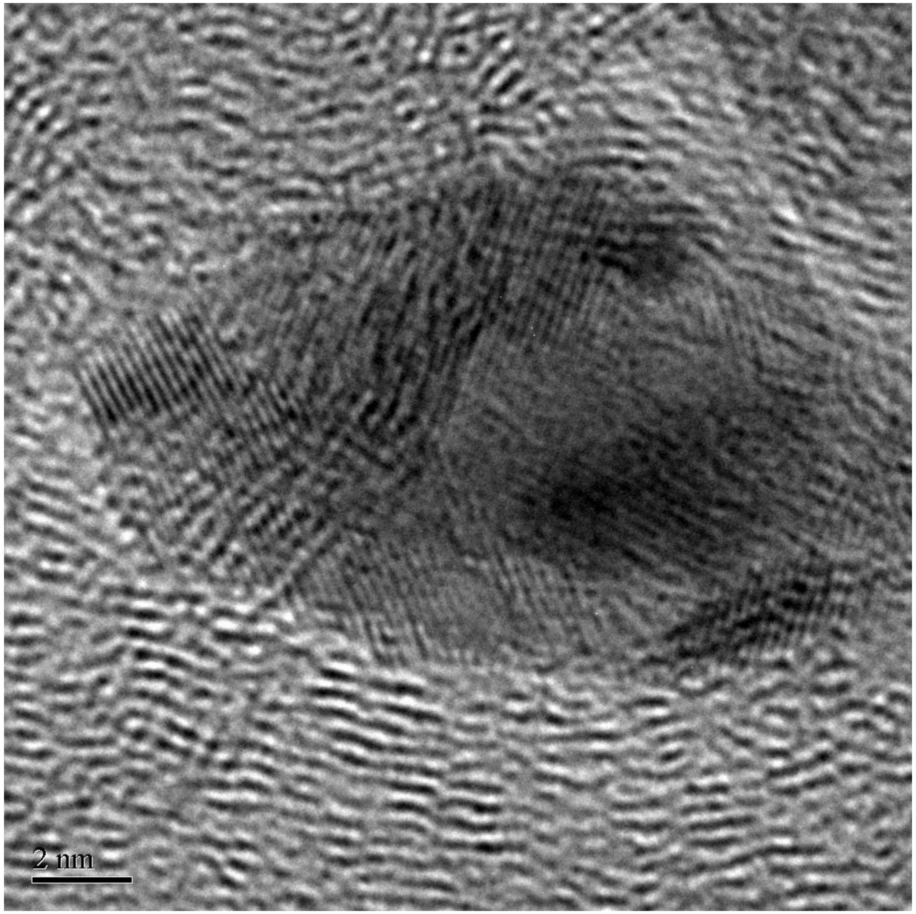


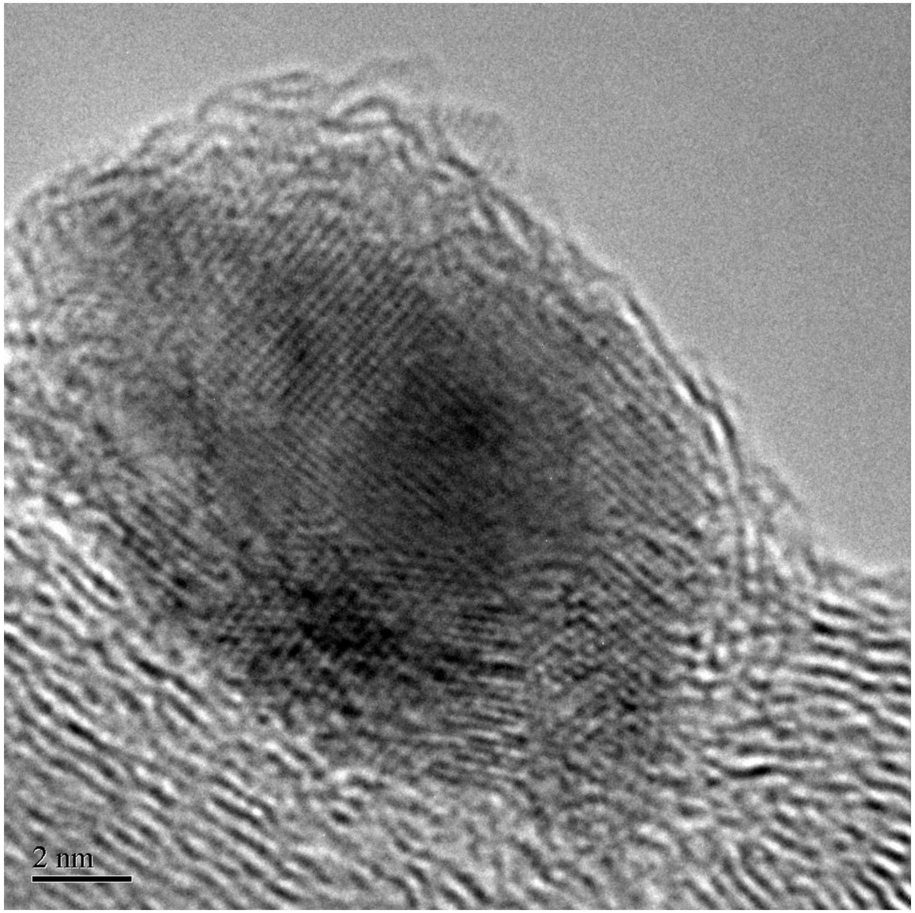
Insertion of hydrogenating metal component and working under hydrogen pressure would improve the catalysts stability and fuel quality



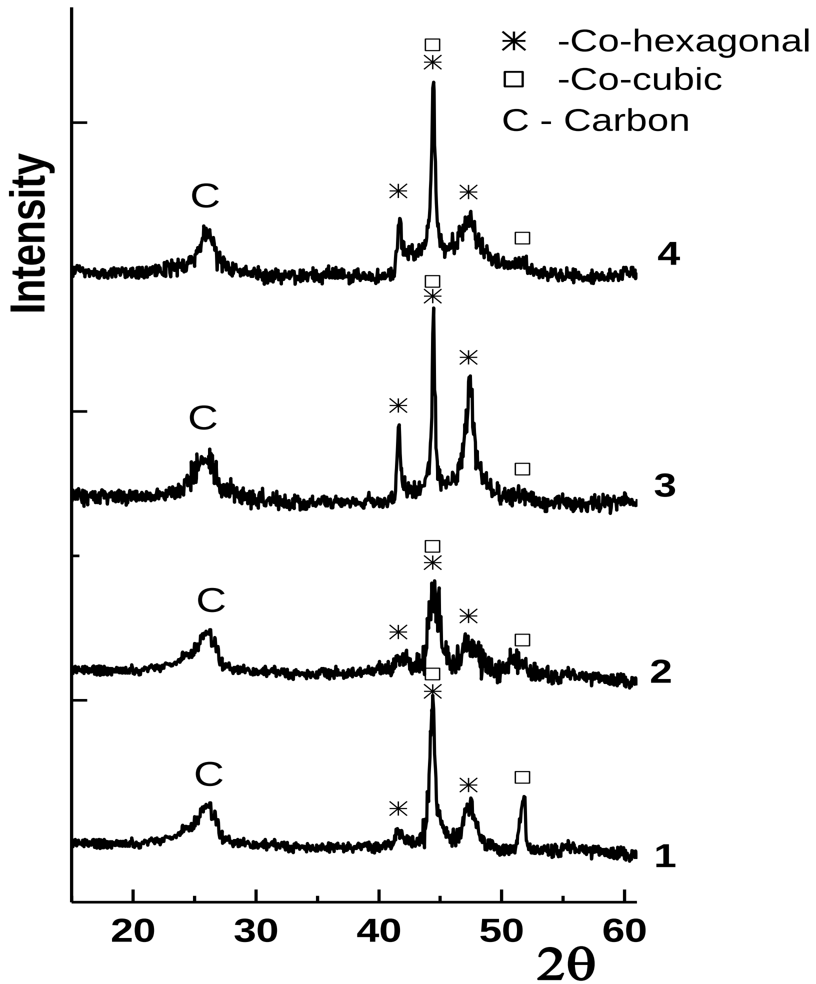
- **1.2 g of C adsorbed to each g of MgO-II catalyst.**

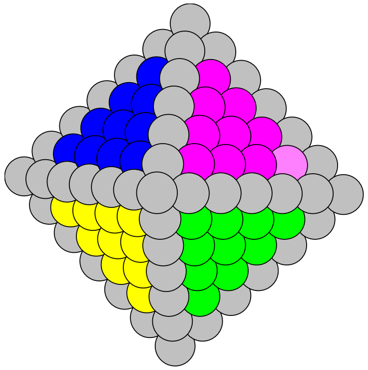
Nanocrystals of metallic cobalt with hexagonal structure were stabilized at the curved surface of air-etched multiwall carbon nanotubes



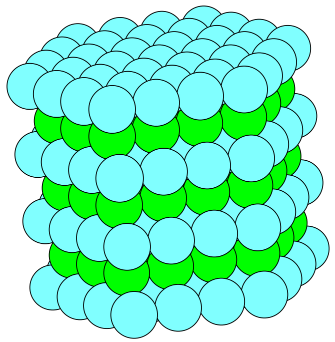


MWCNT modification and Co insertion modes control the exposure of hexagonal Co surface area at constant Co loading of 45 wt.%



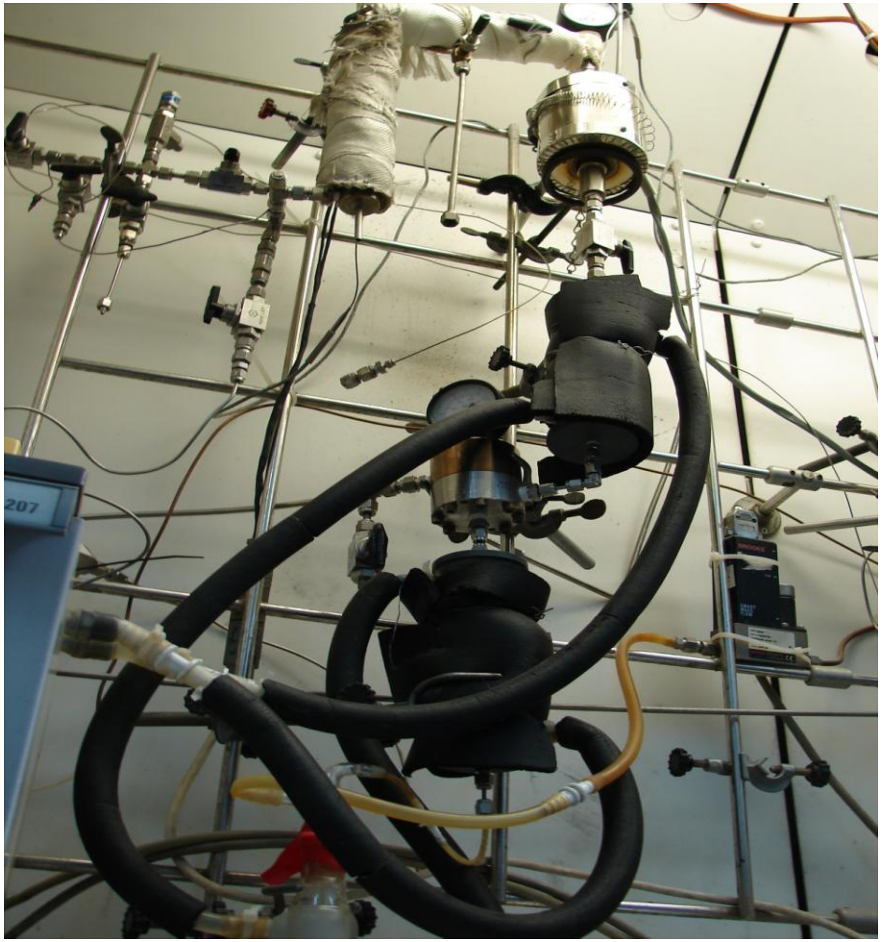


Cubic Co

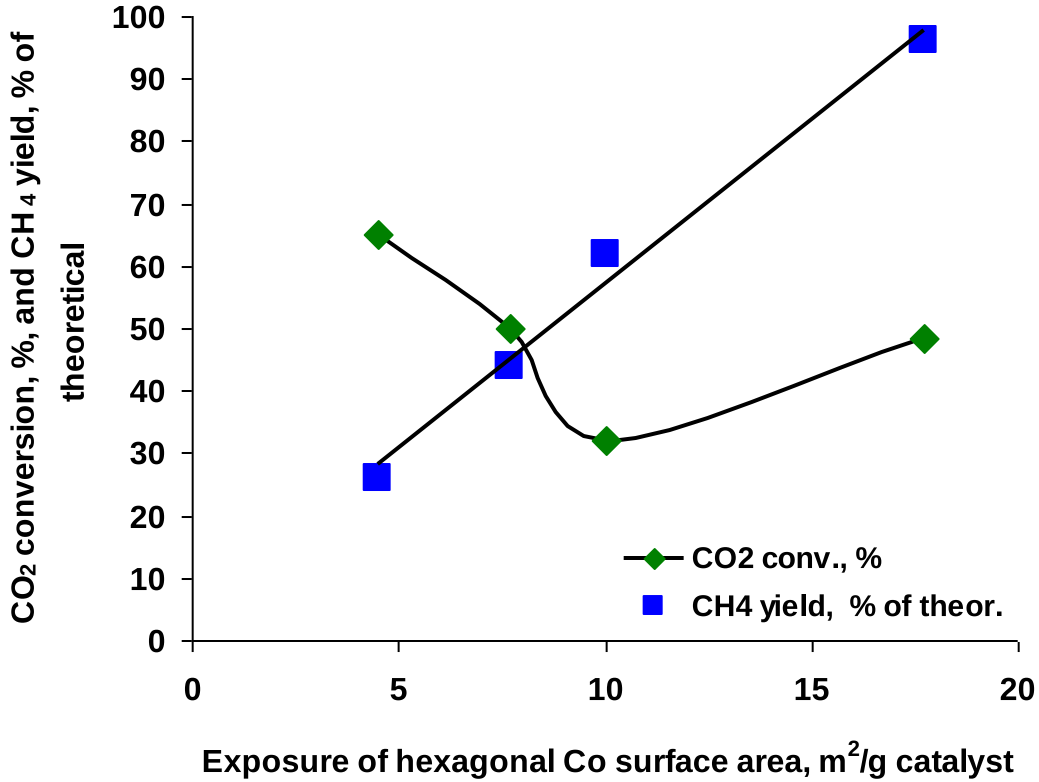


Hexagonal Co

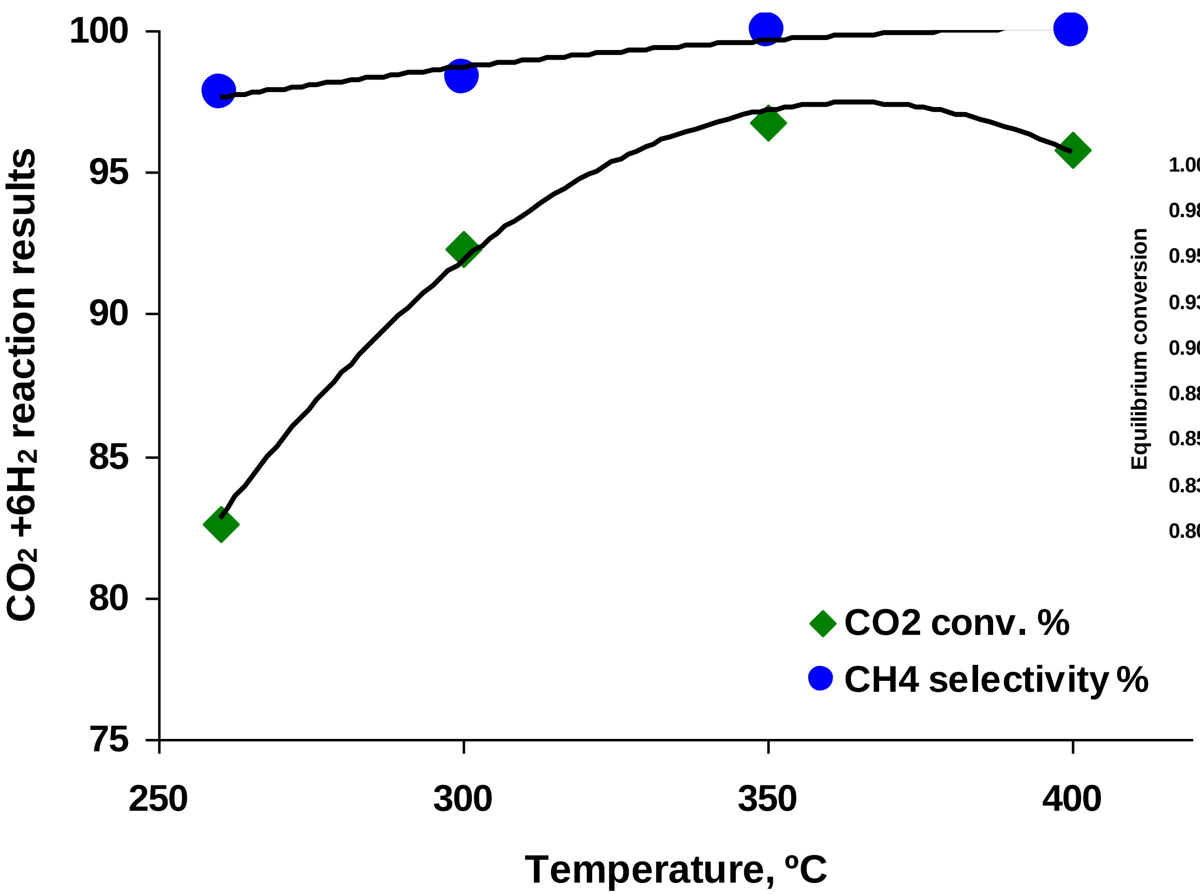
Experimental rig for testing $CO_2+H_2 \rightarrow CH_4$ methanation

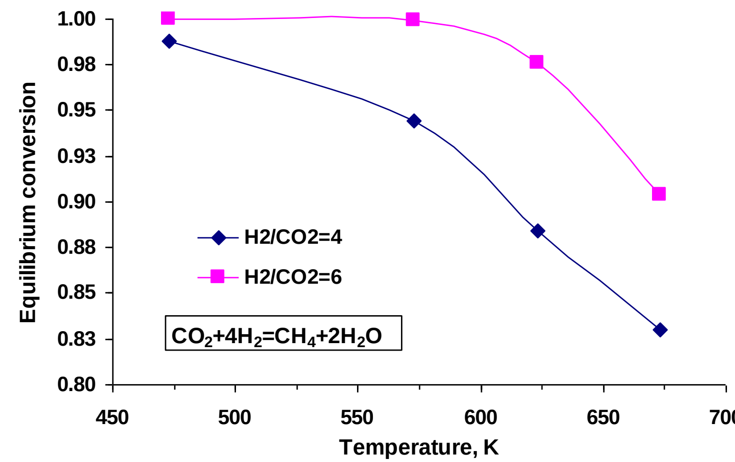


The CH_4 yield in CO_2 methanation at 350ºC, (H_2/CO_2 = 2 GHSV = 5.4 L/g*h) increases proportional to the exposure of hexagonal Co surface



Catalyst with maximal exposure of hexagonal Co surface area display 96% CH_4 yield at 350ºC (H_2/CO_2 = 6, GHSV = 5.4 L/g*h)





Equilibrium CO_2 conversions

Hexagonal Co/MWCNT catalyst shows stable operation at 350°C(H_2/CO_2 = 6, GHSV = 5.4 L/g*h)