ADVANCES IN CATALYSIS FOR HYDROCARBONS

RESULTS FROM ZEOCAT-3D, C123 & BIZEOLCAT EU RESEARCH PROJECTS

ZEOCAT-3D

C123
VALORISING METHANE RESOURCES

BiZeolCat

Funded by
the European Union

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SCALING INNOVATIVE BIZEOLCAT CATALYSTS AND REACTION TESTS TO REACH TRL 5

Cem Aciksari and Serdar Celebi

Turkish Petroleum Refineries (TUPRAS) R&D Center, Kocaeli/TURKIYE

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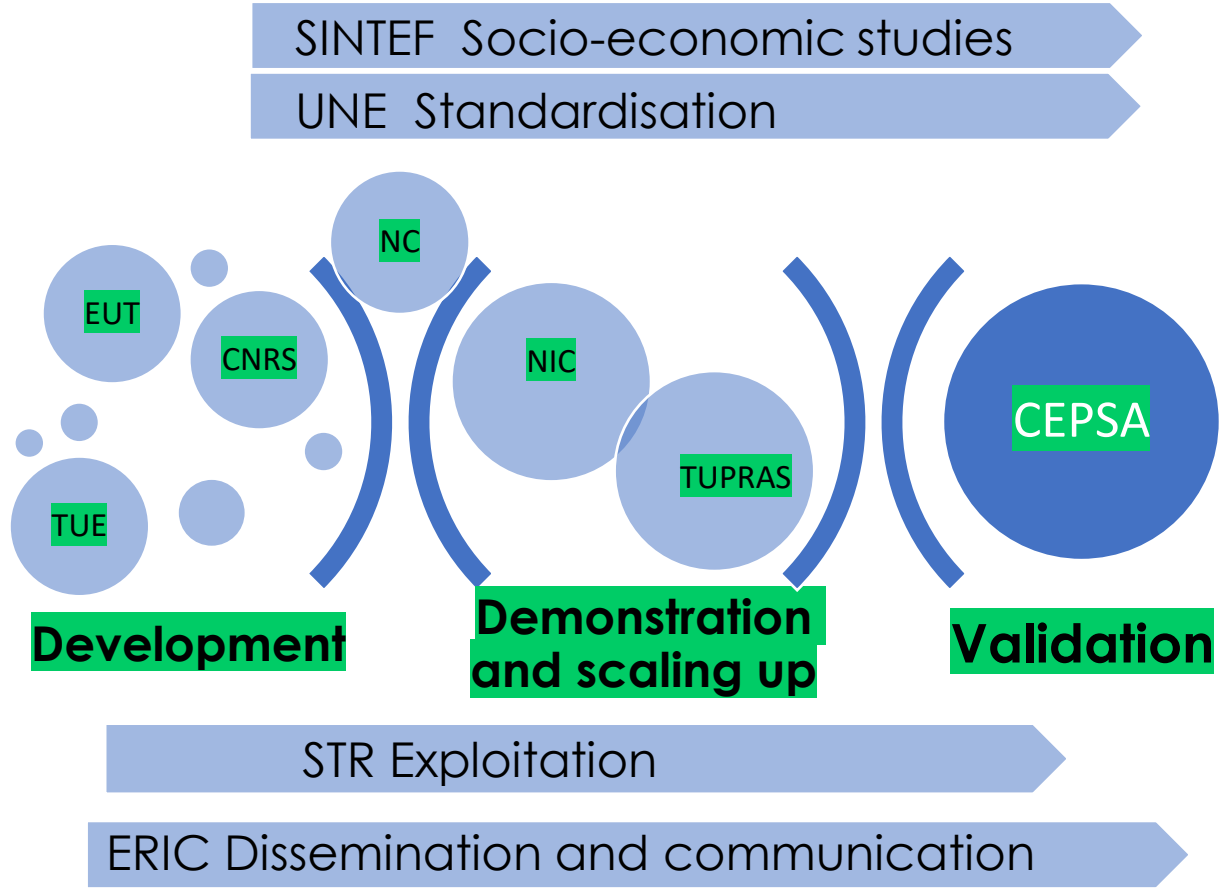
Presentation Outline

- The Main Objectives/Partners and Roles in Bizeolcat Project
- Demonstration and Scaling Up Phases
- Catalyt Scaling up for PDH and BDH
- Catalyt Scaling up for PA reaction
- Pilot Scale Reactor System
- PDH Reaction Performance at Pilot Scale
- PA Reaction Performance at Pilot Scale
- Conclusions for TUPRAS Studies

The Main Objectives/Partners and Roles in Bizeolcat Project

To obtain light olefins and aromatics using light hydrocarbons (C1, C3 and C4) by

- innovative catalysts synthesis methodologies and novel reactor design and processing,
- demonstrating improvement (sustainability and economic scalability) in front of existing industrial processes.



WP 4 – Demonstration and Scaling Up

Leaders: National Ins of Chemistry in Slovenia (main contact) and TUPRAS

Partners involved: EUT, UiO, TuE, SINT, CNRS, TUP, NC, CEPSA

TUPRAS Roles:

- **Task 4.4:** TUPRAS extrudes powder supports that was defined in the development stage of the project and shape them as a pellet form, in order to fabricate the final catalysts for pilot scale unit testing of PDH, BDH and PA reactions.
- **Task 4.5:** TUPRAS performs the industrial-environment pilot-scale fixed-bed reactor (up to 200 ml of catalyst) tests for PDH (propane dehydrogenation processes), BDH (butane/butylene(s) feedstock conversions) and propane aromatization reactions.

T 4.4 – Catalyst Scaling up for PDH and BDH

Final catalyst for PDH and BDH was defined, by technology developers (EUR and CNRS), as:

- **PtSn/Li-Al_2O_3 (Sn/Pt:0.7 wt/wt, Li:0.5% by wt.)***

** The catalyst was prepared by surface orgonometallic approach.*

To reach TRL 5 for catalyst scale-up, activated Al_2O_3 catalyst supports, **mainly y –Al_2O_3 with 0.8 mm in diameter and 3.3 mm in length** have been produced via **Screw Type Extrusion** process.

1st

- AlOOH Paste Preparation
  - **55-60 %** solid loading & gelation with **0.2 M HNO_3**

→
- Targeted mechanical strength
- Maximum extrusion yield

2nd

- Extrusion- Shaping them into cylinders
  - Die diameter **1 mm**
- Breaking up of extrudates into 3 mm in length

3rd

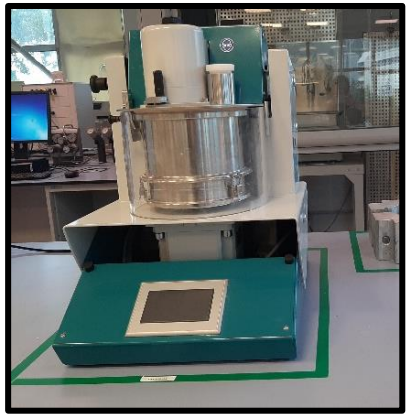
- Drying **@90 °C overnight**
- Heat Treatment
  - Phase transformation from **boehmite** to **gamma @600 °C for 5 h**

→
- Maximum specific surface area
- Optimum pore size and distribution & pore volume

T 4.4 – Catalyst Support Production

Caleva Extruder 3 in 1 machine with a production capacity up 50 g/batch

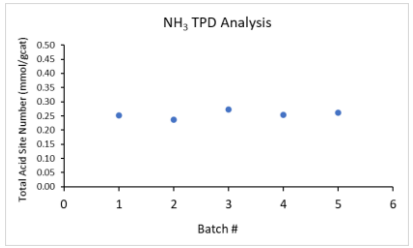
Vinci Mixer with a mixing capacity of 50 g/bacth

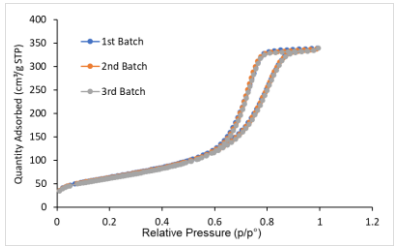


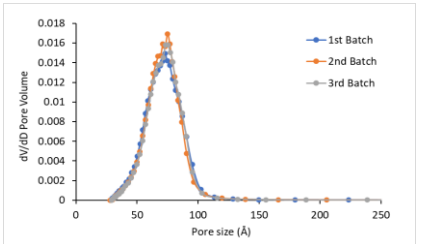
Eirich Granulator with a mixing capacity up to 0.5 kg/bacth

Caleva Extruder machine with a production capacity of 1.0 kg/bacth

	Unit	Value
Al2O3 (XRF by wt.)	[%]	99.8
Phase (XRD)	-	Gamma
Diameter	[mm]	0.8±0.1
Length	[mm]	3.3±0.7
Equivalent Spherical Diameter	[mm]	1.5
Crushing Strength	[N/mm]	35±5
Bulk Density	[g/l]	730
BET Surface Area	[m2/g]	220±10
Pore Volume (BJH Desorp.)	[ml/g]	0.55
Pore Size (BJH Desorp.)	nm	7.5
Total Surface Acidity	[mmol/gcat]	0.26



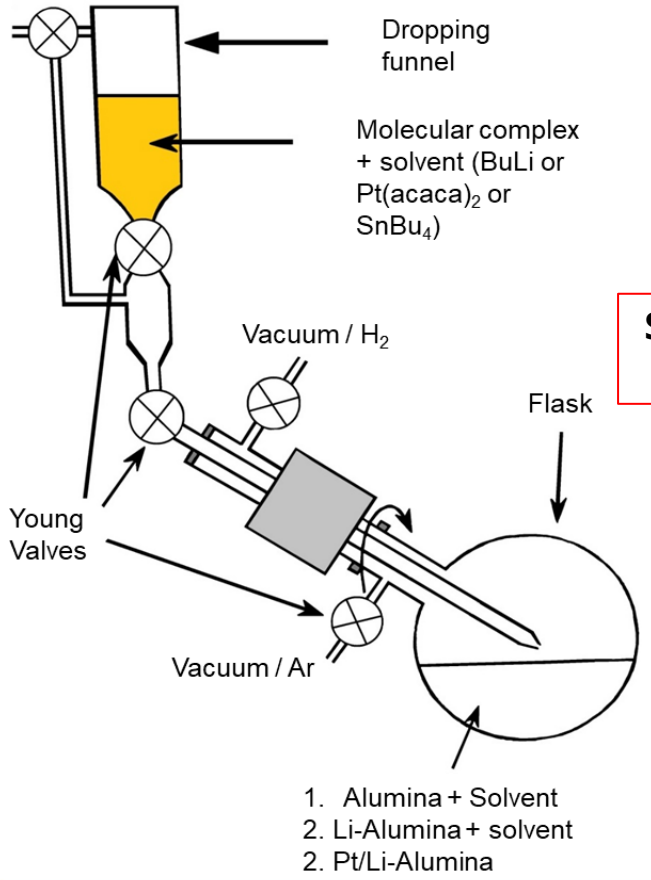




Industrial grade gamma Al_2O_3 catalyst supports were produced to be used for PDH and BDH pilot reaction at TRL 5.

T 4.4 – Metal Impregnation on Shaped Catalyst

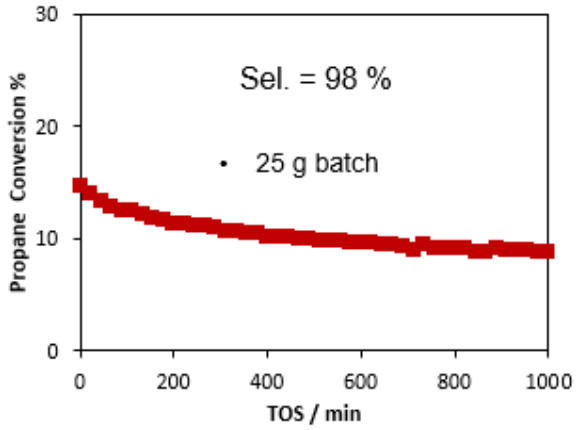
Custom made impregnation set-up developed by CNRS to produce 1 kg final catalyst

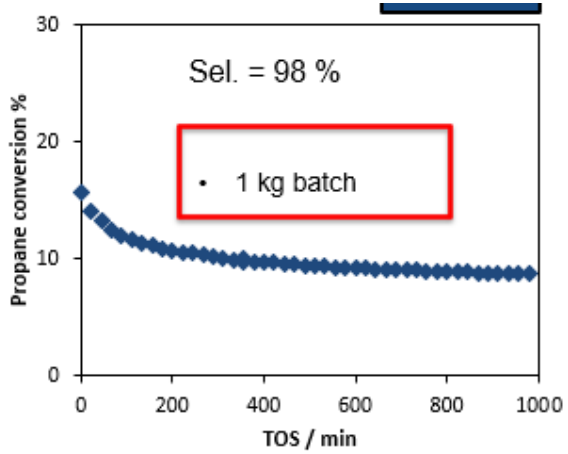


The preparation of the catalysts PtSn/Li-Al_2O_3 from 2 g to 1.1 Kg has been successful completed

	Synthesis batch		
	2g	25 g	**1 kg ***
Li (%wt) by ICP	0.45	0.45	**0.45**
Sn (Sn/Pt) by ICP	0.7	0.7	**0.67 - 0.7**

Similar catalytic performance was observed for the catalysts PtSn supported on Tupras Li-Alumina prepared on large scale and small scale

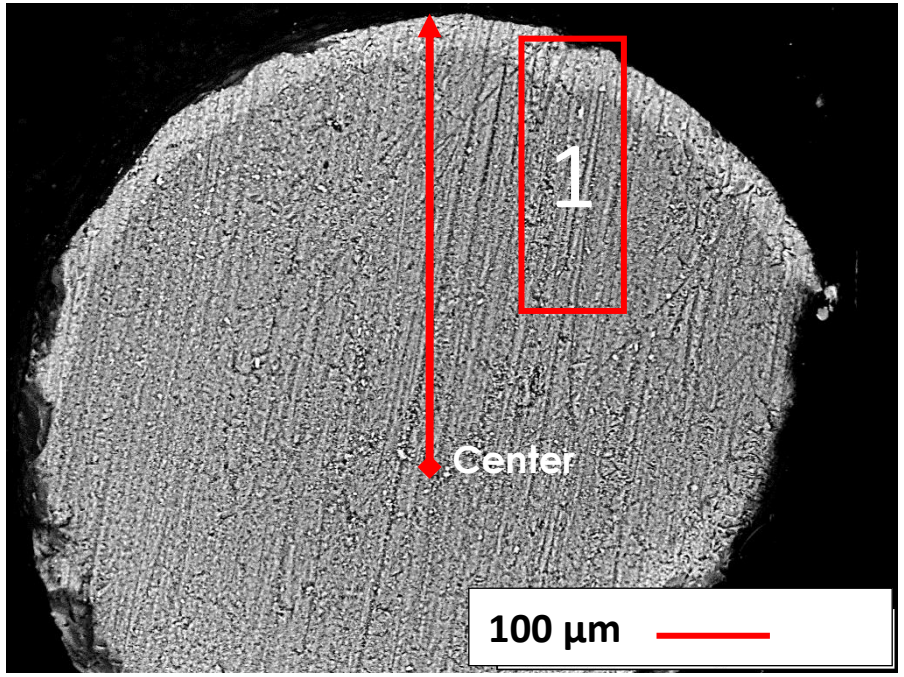




-Temperature of reaction = 530 °C
-Total pressure = 1 bar
- Reaction under H_2 ($3C_3/1H_2/21Ar$)
GHSV = 60000 $mL.g^{-1}.h^{-1}$

T 4.4 – Microstructure of Final PDH Catalyst

The diameter of the catalyst is 800 µm.



PtSn rich layer --> 50 µm

Elemental Analysis of Final Shaped Catalyst

Distance From Surface	Pt	Sn	Sn/Pt
	by wt. %		by at. %
Outer Surface (up to 50 µm)	3.55	1.30	0.6
50 to 100 µm	1.43	0.57	0.7
100 to 200 µm	1.74	0.70	0.67
200 to 300 µm	1.75	0.61	0.56
300 to 400 µm	1.73	0.70	0.67
400 µm	1.75	0.64	0.60
1	**1.90**	**0.86**	**0.75**
ICP	**2.00**	**-**	**0.70**

T 4.4 – Catalyst Scaling up for PA Reaction

Final catalyst for PA was defined, by technology developers (UiO and CNRS), as:

- **Ga/meso-zeolite (Ga:1.0% by wt., Si/Al: 40 by mole)***

** The catalyst support were synthesized by treating of commercial zeolite with NaOH solution to introduce mesoporosity and the final catalyst was prepared by surface orgonometallic approach.*

To reach TRL 5 for catalyst scale-up, meso-zeolite/bentonite composite catalyst supports, have been produced via **Screw Type Extrusion** process.

1st

- Meso-zeolite based paste preparation
  - ➢ **Bentonite up to 25% and solid loading up to 70% by wt.**

→

- Targeted mechanical strength
- Maximum extrusion yield
- Maximum meso-zeolite loading

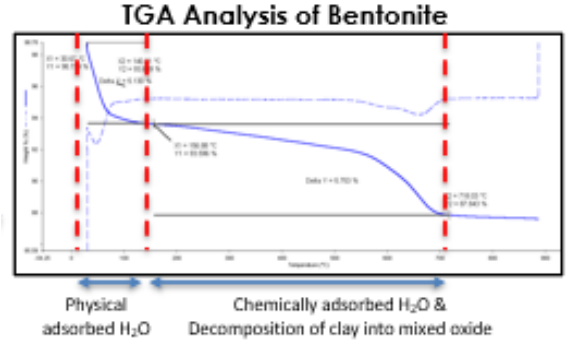
2nd

- Extrusion- Shaping them into cylinders
  - ➢ Die diameter **1.3 mm & Die depth 5.0 mm**
- Breaking up of extrudates into 3 mm in length

3rd

- Drying @**90 °C overnight**
- Heat Treatment
  - ➢ Completion of bentonite transformation to mixed oxide

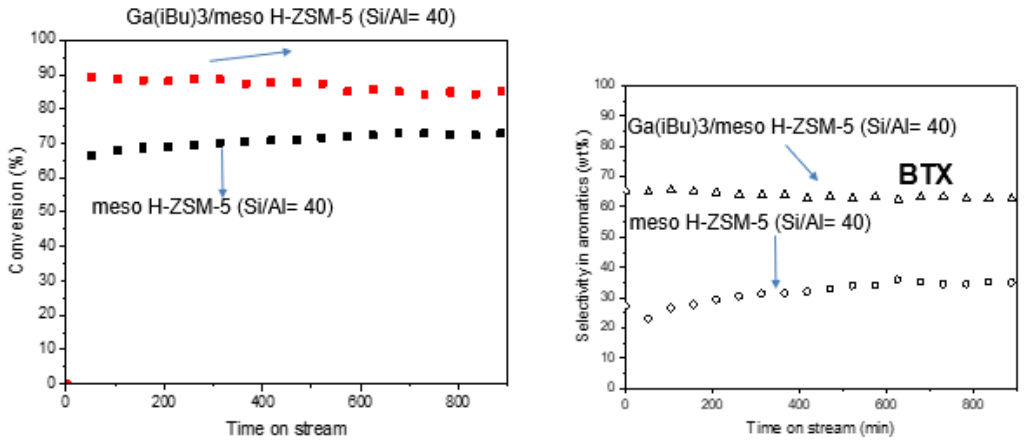
→

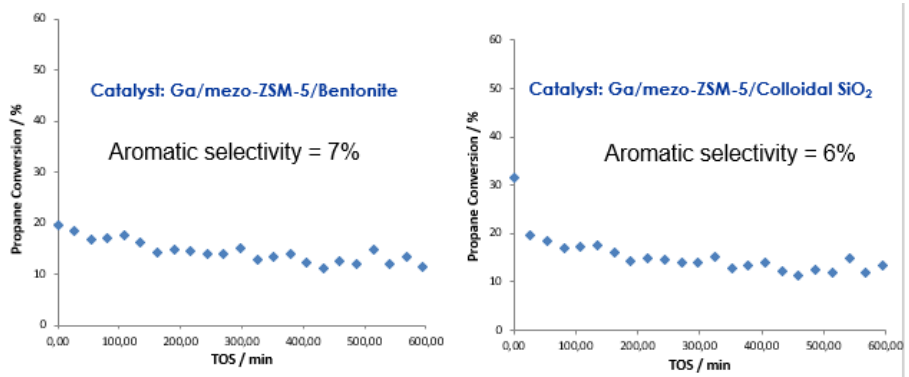


T 4.4 – Catalyst Scaling up for PA Reaction

Propane aromatization performance of best performing powder catalyst composition

Temperature of reaction = 580 °C, Total pressure = 1 bar, Reaction under H_2 ($0.5C_3$/9.5Ar)





2 shaped meso-zeolite supports with different SiO_2 based inorganic binder

Sample Name/ Properties	Col/Meso-zeolite	Bent/Meso-zeolite
Shaping Technique	Extrusion	Extrusion
Diameter (mm) Length (mm)	1.25 3.50	1.25 4.00
Inorganic binder (%), by wt	25	25
Organic binder (%), by wt	3.0	2.5
Calcination T (°C)	550	700
Crushing Strentgh (N/mm)	20 ± 4	22 ± 5
BET Surface Area (m^2/g)*	330	300

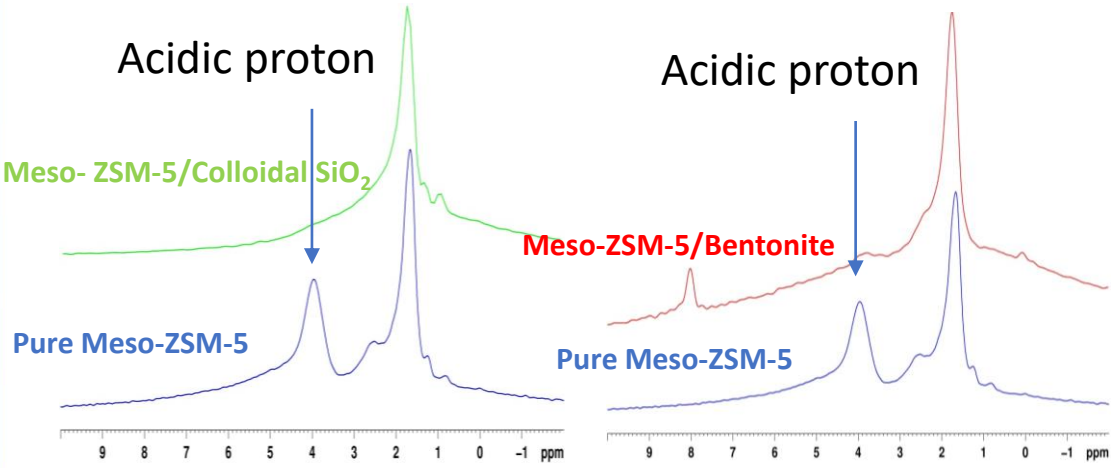
* BET of Meso-zeolite powder is 420 m^2/g

Low activity and selectivity is obtained by the shaped supports meso-ZSM-5 with bentonite or colloidal silica

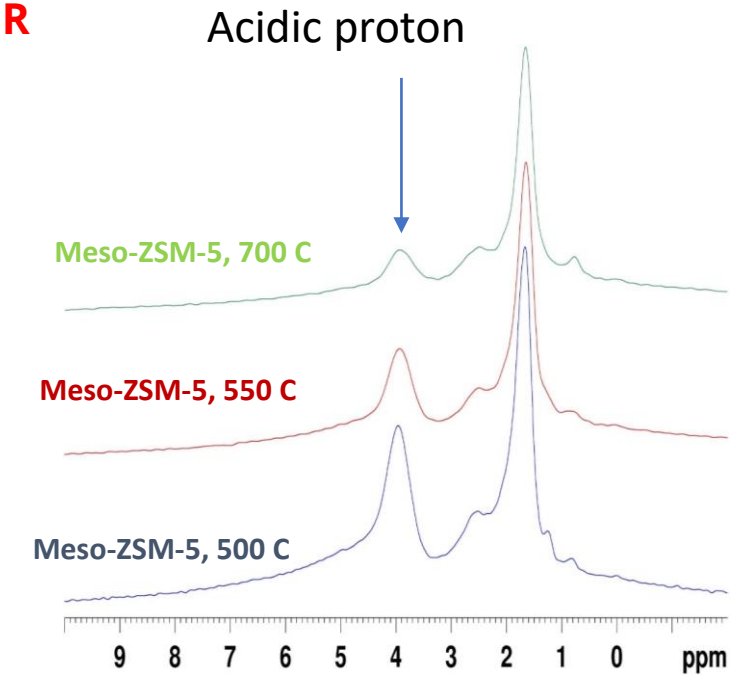
T 4.4 – Catalyst Development for PA Reaction

The low activity and selectivity are attributed to the low acidity in both shaped supports

1H Solid State NMR



The effect of bare meso-zeolite powder calcination temperature on acidity oof the support

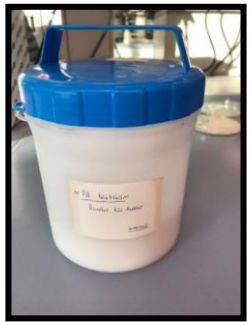


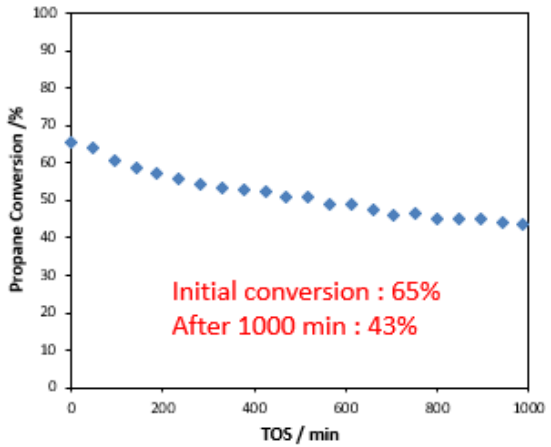
The calcination at 700 °C to complete bentonite transformation into mixed oxide is undesirable due to a decrease of acidic proton at 4 ppm

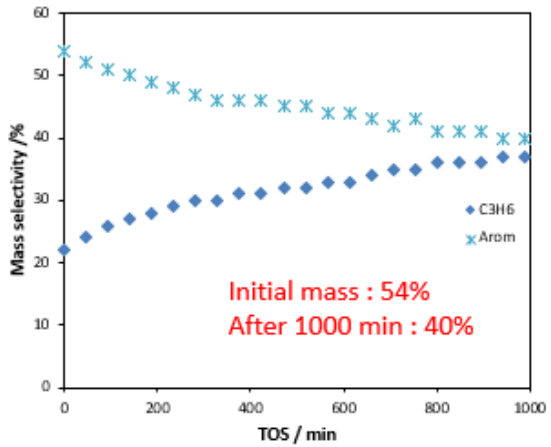
T 4.4 – Catalyst Development for PA Reaction

The Goal is to reduce the amount of inorganic binder and calcination temperature in order to improve the catalytic activity.

	Unit	Result
Composition (SEM-EDX) SiO_2 Al_2O_3 Fe_2O_3 MgO	% wt.	 95.0±0.5 4.25±0.25 0.45 0.30
Ga, (ICP)	% wt.	0.91
Phase (XRD)	-	Zeolitic structure
Diameter	[mm]	0.8±0.1
Length	[mm]	3.0±0.5
Equivalent Spherical Diameter	[mm]	1.5
Crushing Strength	[N/mm]	9±2
Bulk Density	[g/l]	~700
BET Surface Area	[m^2/g]	350±10
Pore Volume (BJH Desorption)	[ml/g]	0.23
Pore Size (BJH Desorption)	[nm]	6.0
Binder Type	-	Bentonite
Binder Amount	% wt.	~15

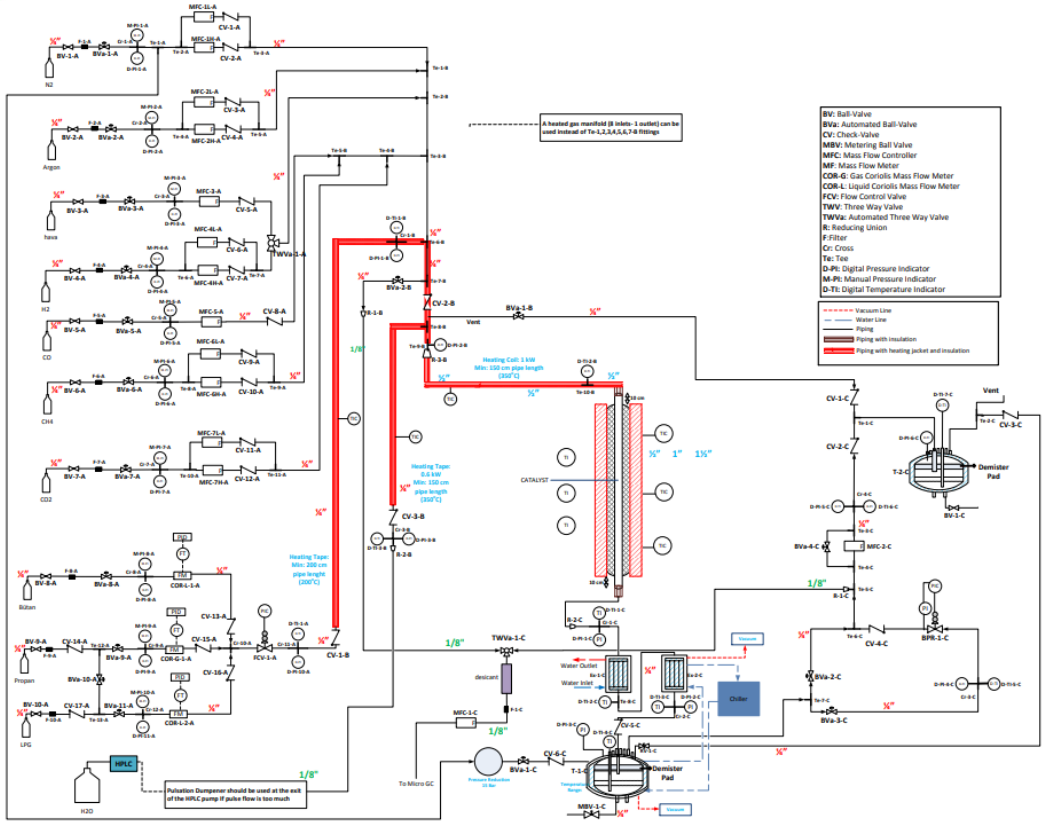






For the final PA shaped catalyst, the selectivity towards aromatics reached 55 % as the Ga loaded meso-zeolite powder has BTX selectivity of 65%. The conversion was calculated as 65% (powder was around 80%).

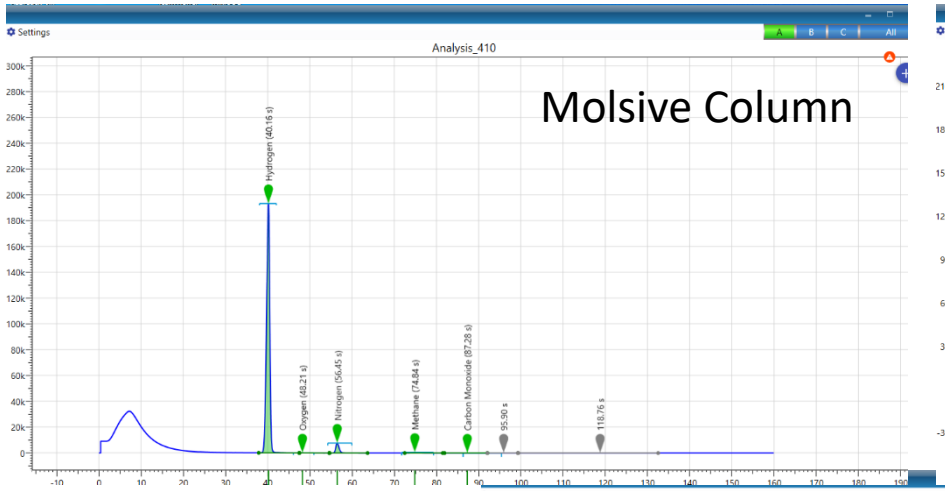
T 4.5 – Pilot Scale Reactor System

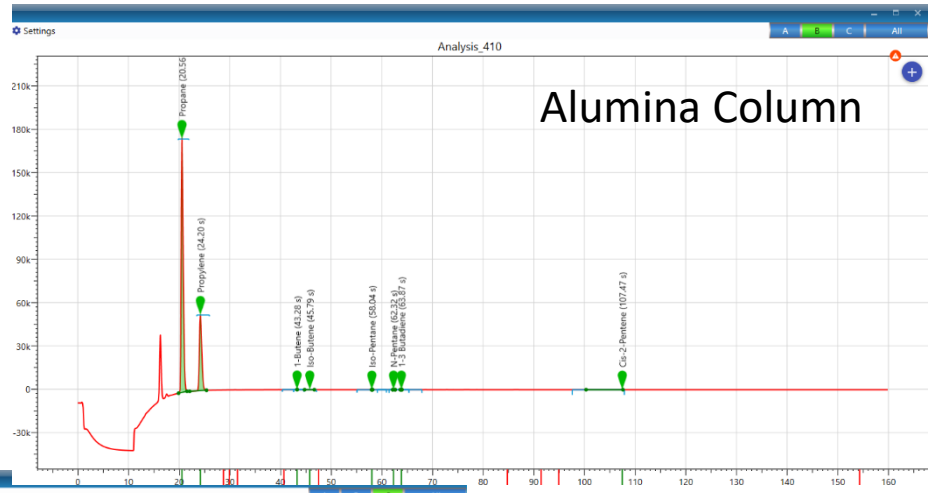


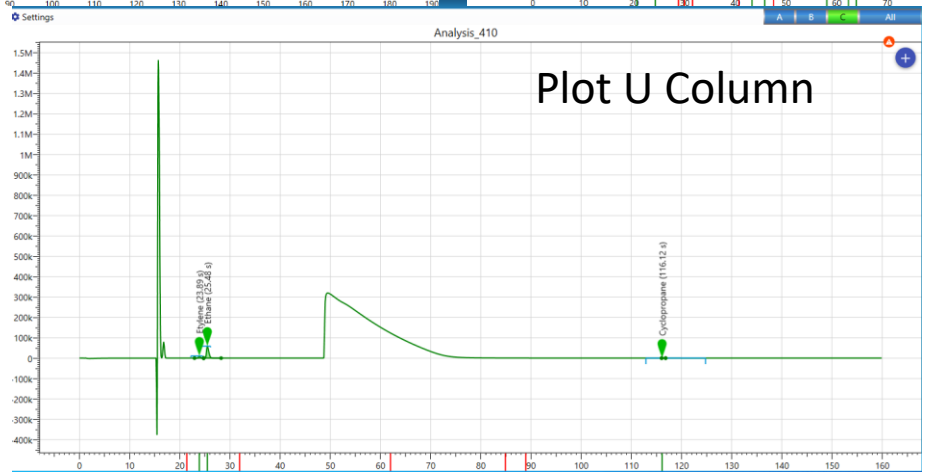
A pilot scale reactor system is designed to operate the following reactions:
Dehydrogenation, Dehydroaromatization, Fischer Tropsch, Reforming Hydroformylation and Hydroprocessing

BiZeolCat

MicroGC







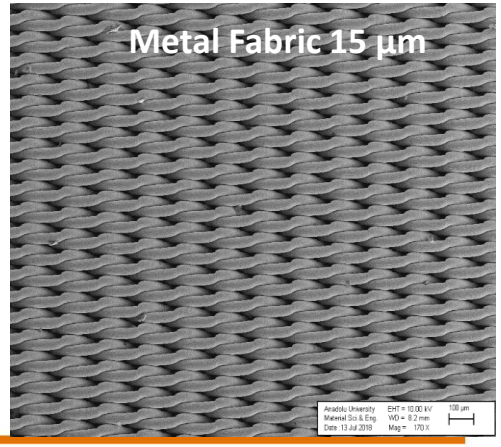
Micro GC with 3 columns
HCs C1-C6
N2, O2, H2, CO

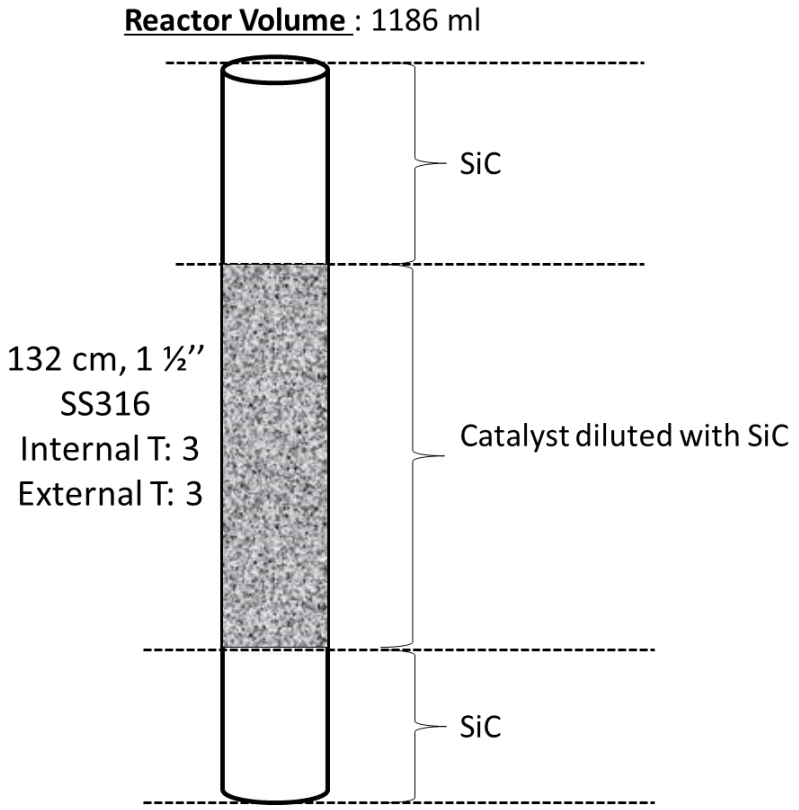
T 4.5 – Pilot Scale Reactor System

Considerations in scale up from lab scale to pilot scale

- Similar WHSV levels
- Catalyst loading amounts and loading scheme
- Reasonable feed compositions in terms of industrial pow
- Dilution of feed with internal standart for GC calculations
- Control of catalyst bed temperature

Catalyst Loading





T 4.5 – PDH Reaction Performance at Pilot Scale

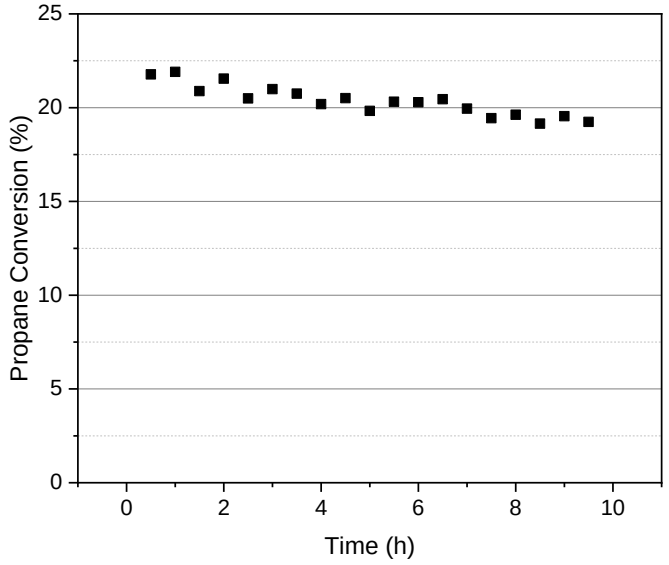
Test Run with 12.5 gr catalyst

Feed composition by volume: N_2 (% mole): 20, Propane/H_2 mole ratio = 3

Condition	Value
Ext T (C)	590
Int T (C)	530
Cat (g)	12.5
N2 (ml/min)	130
N2 (gr/hr)	9.75
Propane (gr/h)	61
H2 (ml/min)	172
H2 (gr/h)	0.93
Mass Flow (gr/h)	71.7
WHSV h^{-1}	5.73

Propane Density= 24 kg/m^3

@ 25 °C, 8 bar

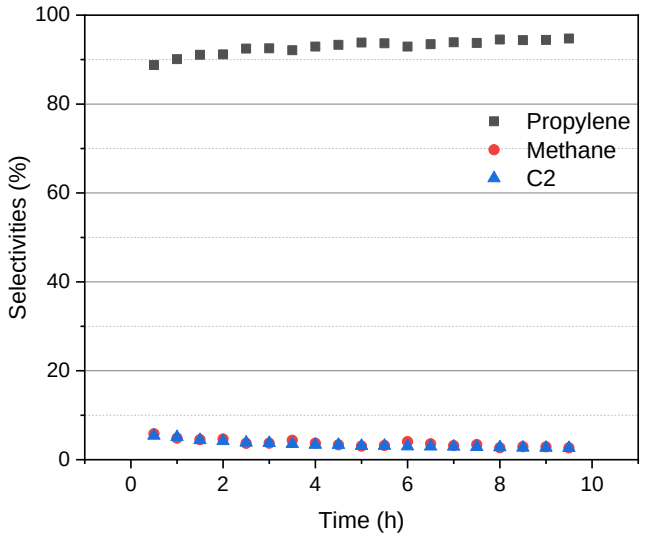


Conversion from 22% to 19% in 9.5 hours

$$Selectivity = \frac{Propylene\ in\ exit}{Propylene+C1+C2\ in\ exit}$$

At the end of 9.5 h operation

- Propylene – 94.7%
- C2 – 2.6%
- Methane – 2.6%

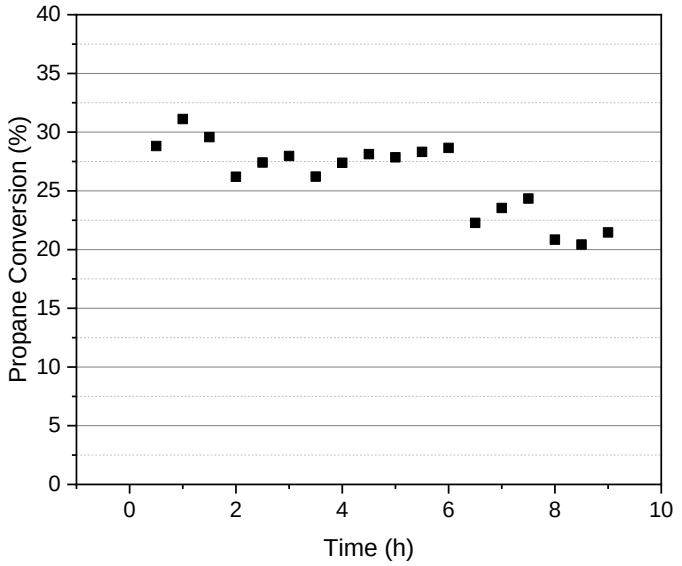


T 4.5 – PDH Reaction Performance at Pilot Scale

Test Run with 125 g (175 ml) catalyst

Feed composition by volume: N_2 (% mole): 20, Propane/H_2 mole ratio = 3

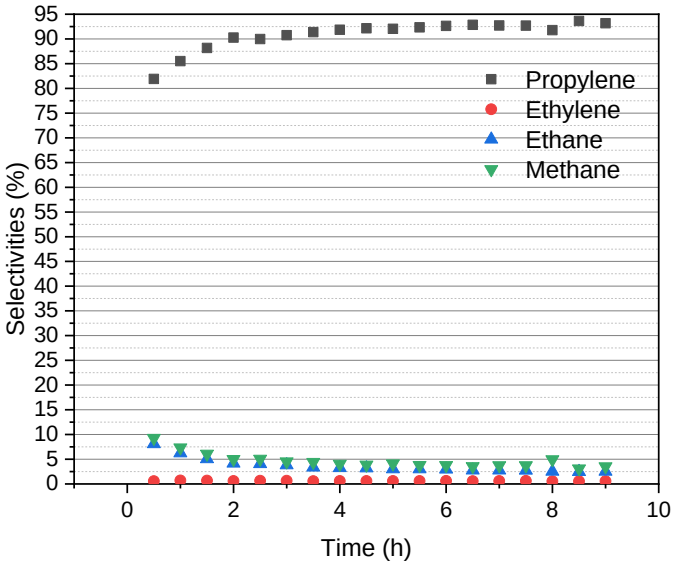
Condition	Value
Ext T (C)	590
Int T (C)	530
Cat (g)	125
N2 (ml/min)	1300
N2 (gr/hr)	97.5
Propane (gr/h)	610
H2 (ml/min)	1720
H2 (gr/h)	9.3
Mass Flow (gr/h)	717
WHSV h^{-1}	5.73



Conversion from 30% to 21% in 9 hours

At the end of 9 h operation

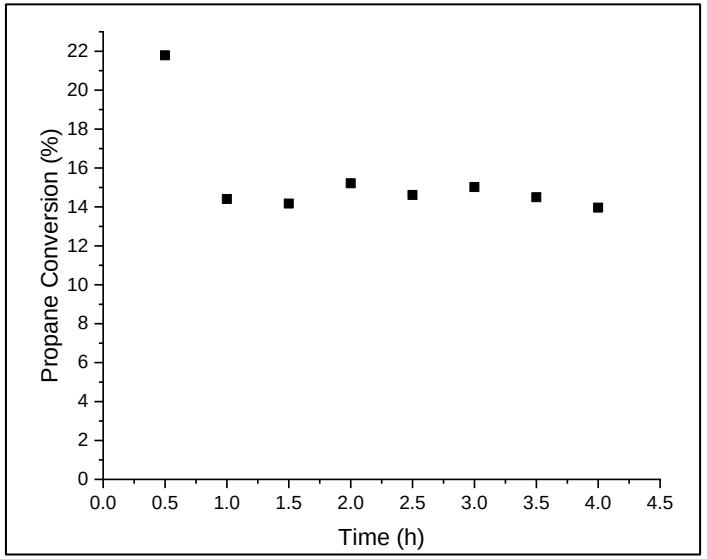
- Propylene – 93%
- C2 – 3%
- Methane – 3.5%

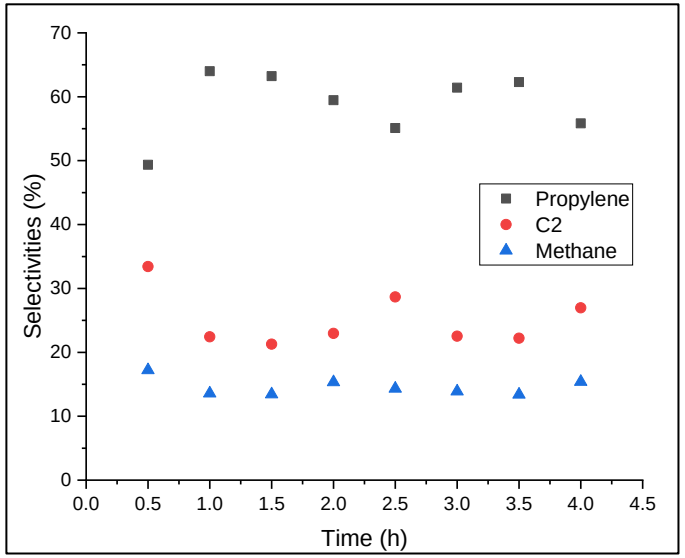


T 4.5 – PA Reaction Performance at Pilot Scale

Feed composition by volume: N_2 (% mole): 95, Propane (% mole): 5

Condition	Value
Ext T (C)	625
Int T (C)	580
Cat (g)	42
N_2 (ml/min)	1000
Propane (gr/h)	72
Mass Flow (gr/h)	147
WHSV h^{-1}	3.50





Just a couple of droplets of liquid product observed!

Probably due to GaN_x formation in the existence of N_2 at high temperatures

T 4.5 – PA Reaction Performance at Pilot Scale

Condition	Value
Ext T (C)	625
Int T (C)	580
Cat (g)	51
Ar (ml/min)	1000
Propane (gr/h)	72
Mass Flow (gr/h)	179
WHSV h^{-1}	3.50

Since Ar is not detected by MicroGC, it is not possible to calculate conversion accurately

Benzene concentration is decreasing with time!!!

Feed (excluding Ar) → 100% Propane

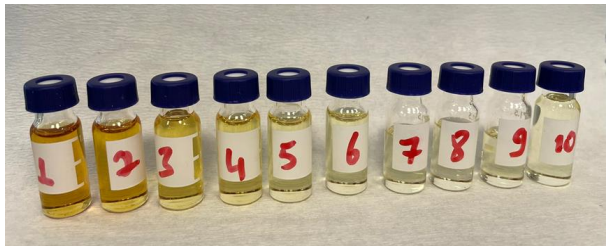
Gaseous product (excluding Ar) → 75% Propane
14% H_2
6% Propylene
1.5% CH_4

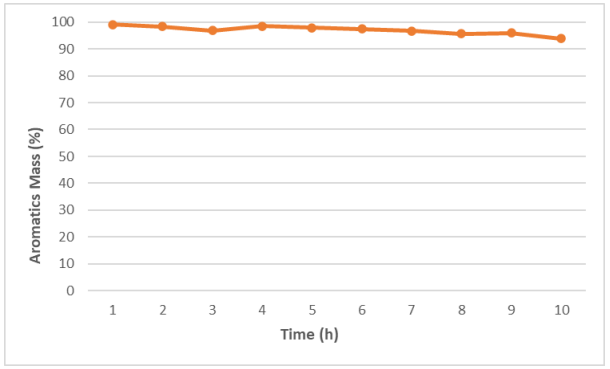
Liquid product → ~7.7 gr product from 288 gr Propane in 4 hrs

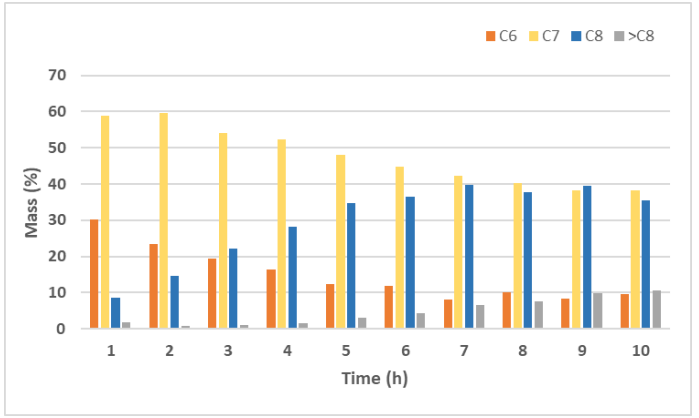
T 4.5 – PA Reaction Performance at Pilot Scale

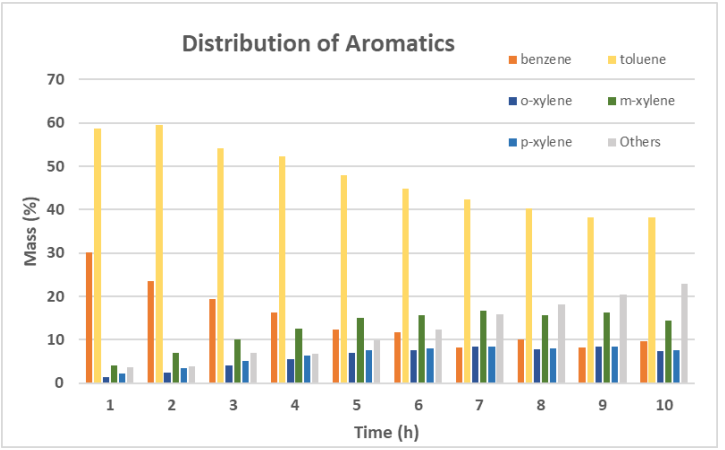
Feed composition by volume: Ar (% mole): 95, Propane (% mole): 5

Condition	Value
Ext T (C)	625
Int T (C)	580
Cat (g)	51
Ar (ml/min)	1000
Propane (gr/h)	72
Mass Flow (gr/h)	179
WHSV h^{-1}	3.50



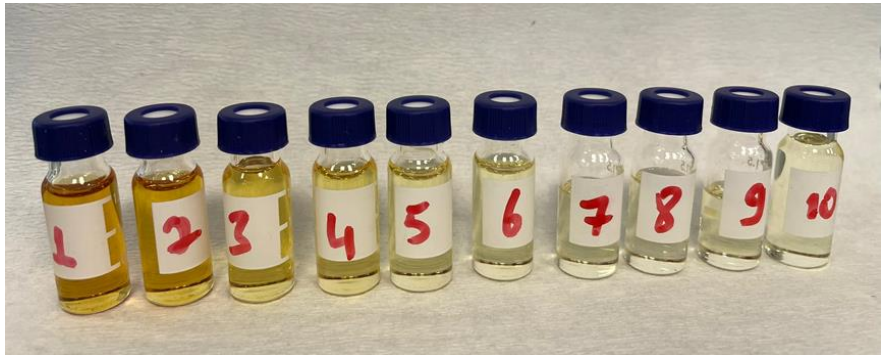






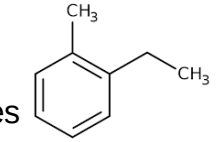
- Total aromatic mass concentration is always above 95 %.
- Benzene and toluene mass concentrations decrease with time.
- Xylene mass concentrations increases with time
- m-xylene (Thermodynamically most stable) is dominant among the other xylenes.
- Steady state behaviour is obtained after 8 hours. Concentrations are getting stable.

T 4.5 – PA Reaction Performance at Pilot Scale

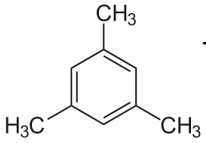


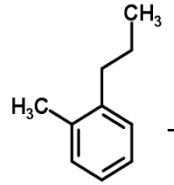
- Ethyl Toluene (1,3 methylethyl benzene) and trimethyl benzenes are dominant in C9.
- Propyl Toluene specifically 1,2 methyl-isopropyl benzene is dominant in C10.

Ethyl Toluenes

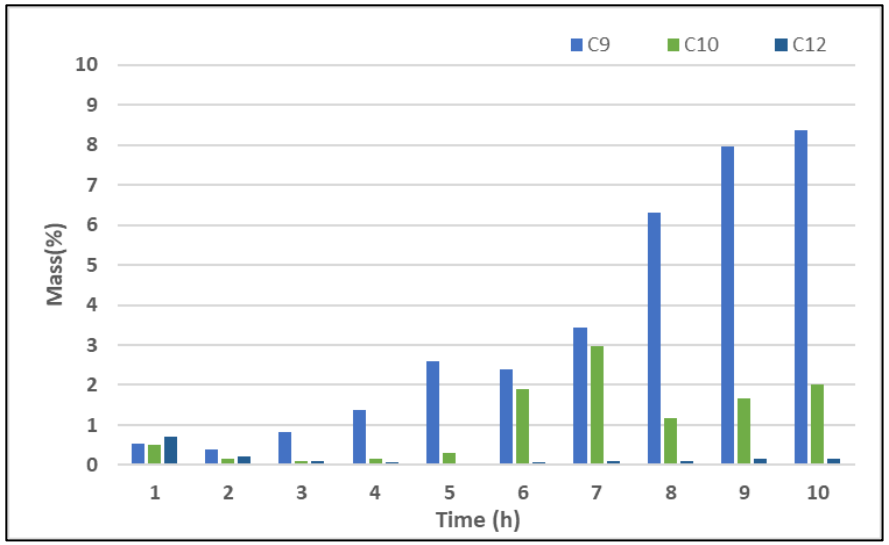


Tri-Methyl Benzenes

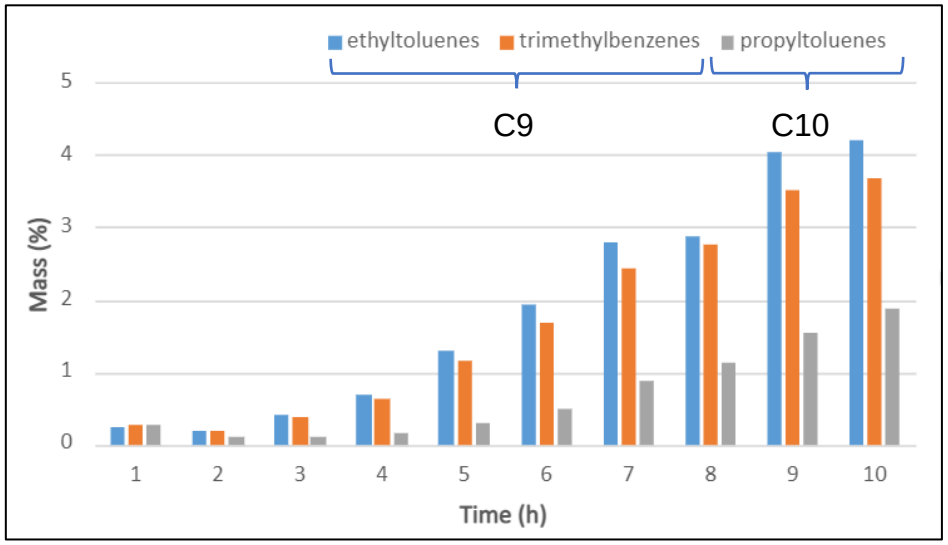




Propyl Toluenes



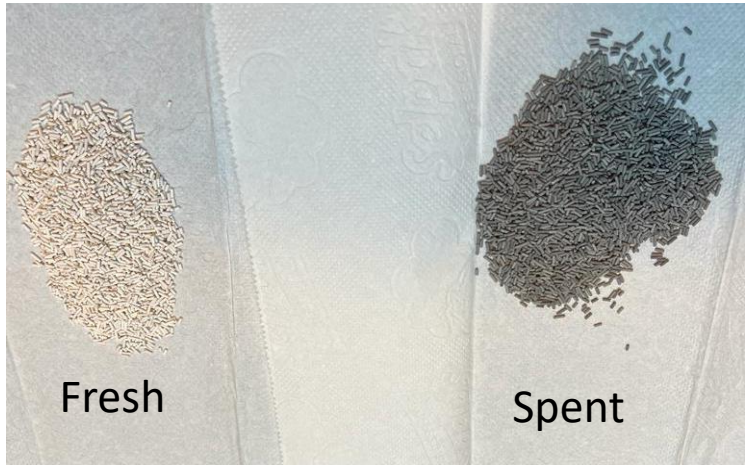
PIONA Reformulyzer Result (Group Analyses)

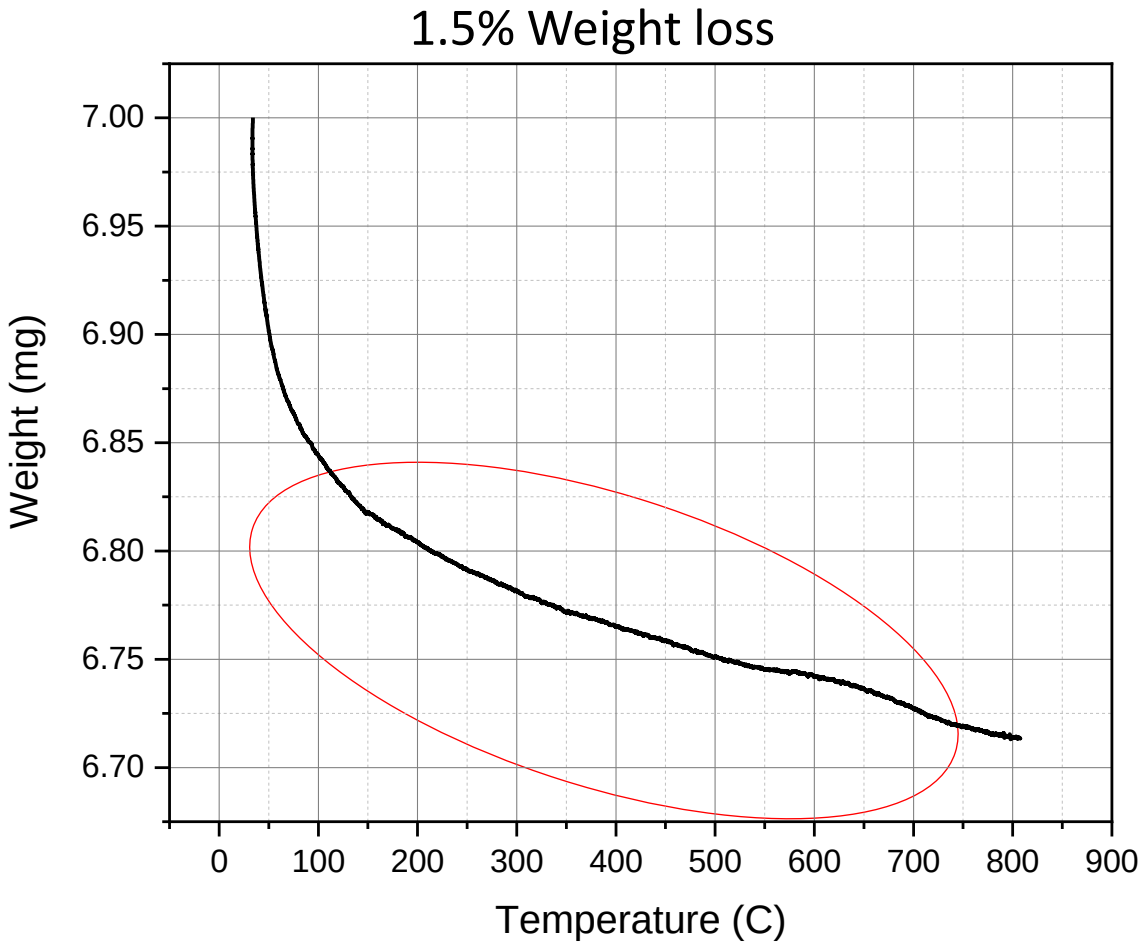


DHA (detailed hydrocarbon analyses)

T 4.5 – PA Reaction Performance at Pilot Scale

TGA result on spent catalyst





Conclusions for TUPRAS Studies

- PDH, BDH, and PAr catalyst scale-up has been completed in collaboration with the technology developers.
  - The best performing PDH and BDH catalyst and its performance shown below:
    - The catalyst support was shaped via extrusion process starting from AlOOH particles.
    - PDH conversion was around 10% at 1000 min and the selectivity was 98%.
  - The best performing PA catalyst and its performance shown below:
    - The catalyst support was shaped via extrusion process starting from meso-zeolite particles synthesized by UiO.
    - Ga/85meso-zeolite/15bentonite (Ga: 1.0 by wt., Si/Al: 40 by mole, support consists of 85% of meso-zeolite and 15% of bentonite by w.t)
    - For the final PA catalyst, the selectivity towards aromatics reached 55 % as the Ga loaded meso-zeolite powder has BTX selectivity of 65%. The conversion was calculated as 65% (powder was around 80%).
- In PDH pilot scale reaction tests(12.5 gr & 125 gr catalyst), similar performance results with lab scale by CNRS has been observed in conversion and selectivities.
- In PAr pilot scale reaction tests (60 gr), aromatics in liquid has been produced when feed is diluted with 95 vol% Ar. N_2 most probably deactivates the catalyst.

THANK YOU

Contacts:

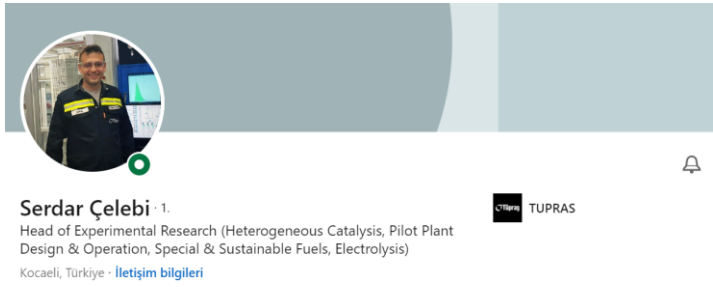
Cem Aciksari and Serdar Celebi from TUPRAS

Ana Villacampa Del Tiempo from EUROCAT

cem.aciksari@tupras.com.tr

serdar.celebi@tupras.com.tr

ana.villacampa@eurecat.org



linkedin.com/in/cemaciksari

linkedin.com/in/serdar-celebi