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

These projects have received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement Nos. 814548, 814671 & 814557

Sustainable olefins and aromatics by innovative nanocatalysts

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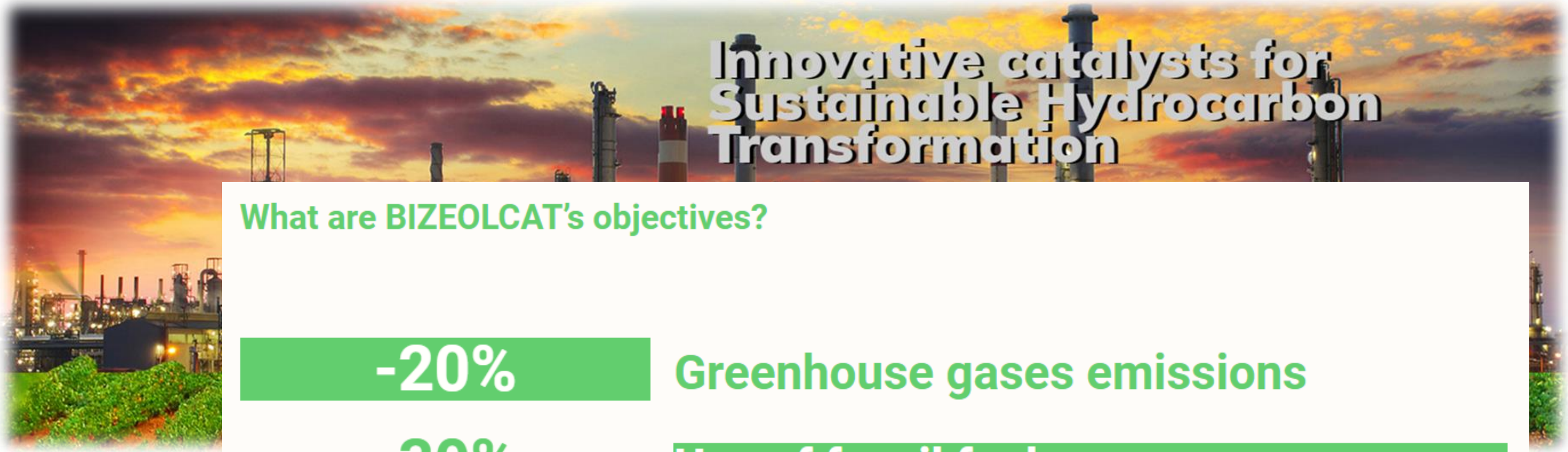
Fundació Eurecat, Centre Tecnològic de Catalunya,

Unitat de Tecnologia Química (UTQ)

BIZEOLCAT Introduction: Challenge



What are BIZEOLCAT's objectives?

-20%	Greenhouse gases emissions
-30%	Use of fossil fuel
-20%	Energy consumption
-20%	Investment costs

https://cordis.europa.eu/project/id/814671/es

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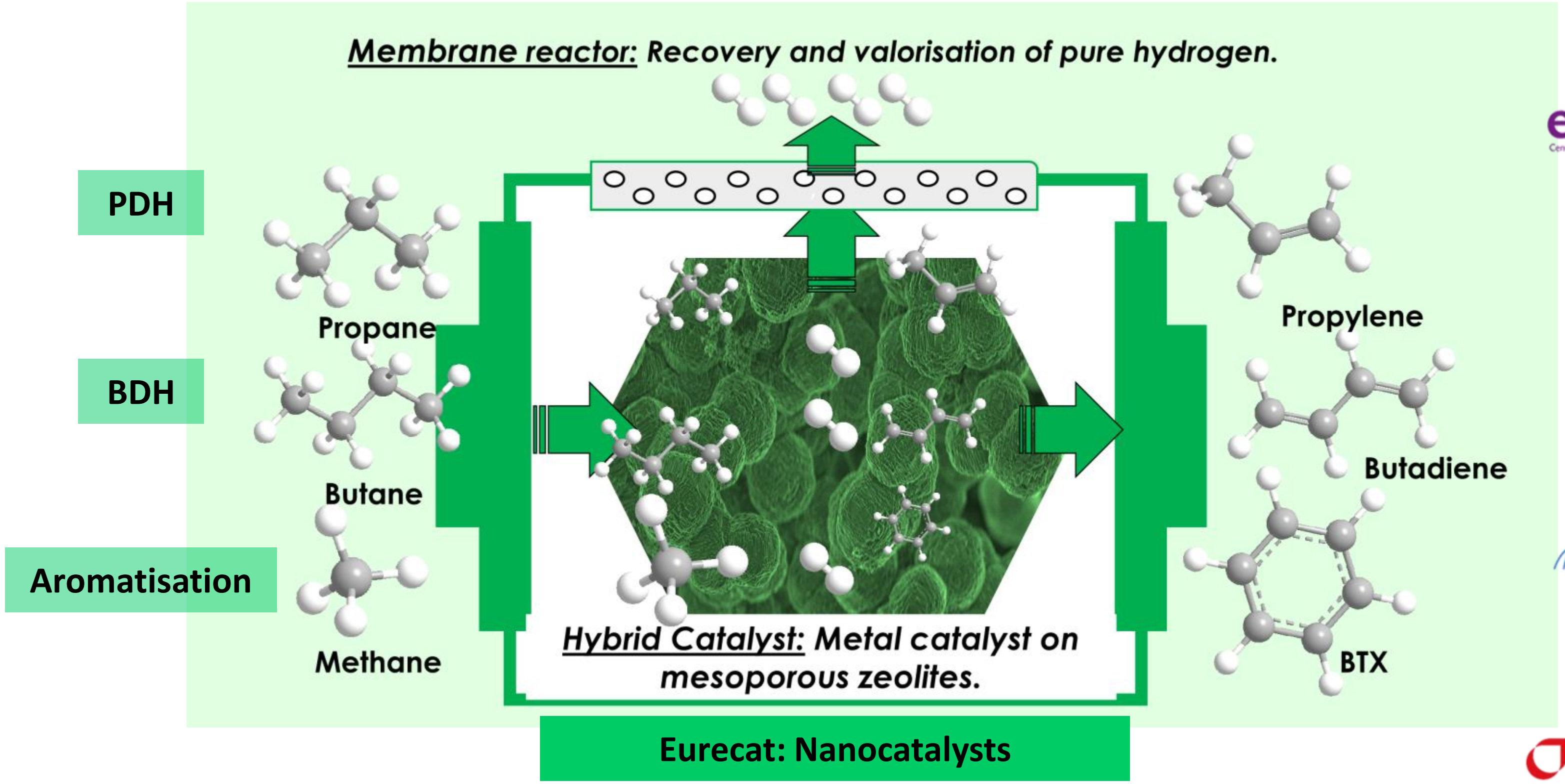

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Target molecules

BTX

Polyester

Polyurethane

Polystirene

They are
Building blocks!

Increasing
Demand

Propylene

Polyacrylonitrile

Polypropylene

Polyisoprene

1,3-Butadiene

SBS, SBR

ABS

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Target molecules

Propylene

1,3-Butadiene

BTX

Naphta
Cracking

Alternatives!

- Propane Dehydrogenation (PDH)
- Butane/Butene Dehydrogenation (BDH)
- Propane aromatization (PAr)

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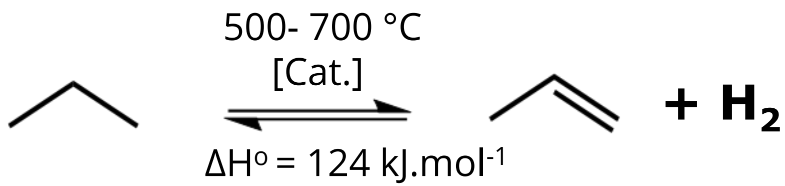
BiZeolCat Target molecules: Benchmark Technologies

• Propane Dehydrogenation (PDH)



- Breaking 2 C-H bonds
- Release alkene and H_2
- Highly endothermic
- Equil. conversion

Catalyst : CrO_x/Al_2O_3 Cr (18-20 wt%)

Catofin®:
T= 590-650 °C
P= 0.2 and 0.5 bar
Conv. of 48-65 %, Sel. of 82 %
Cycle time: 15-30 min

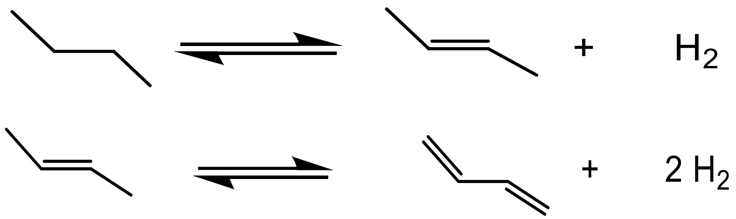
Catalyst : $Pt\text{-}Sn/Al_2O_3$

Oleflex®:
T= 525-705 °C
P= 1 to 3 bar
Conv. of 22-70 %, Sel. 85%
Cycle time: 15-30 min

• Butane/Butene Dehydrogenation (BDH)

Catalyst : CrO_x/Al_2O_3 Cr (18-20 wt%)

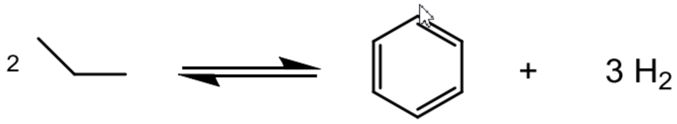
Catadiene®
T= 600-620 °C
P= 0.2 and 0.4 bar of C4
Conv. 30-40 %, Sel. of 60%
(2 steps are required)



• Propane aromatization (PAr)

Catalyst : Ga/Zeolite

Cyclar®
T= 550-650 °C
Sel. of 63%



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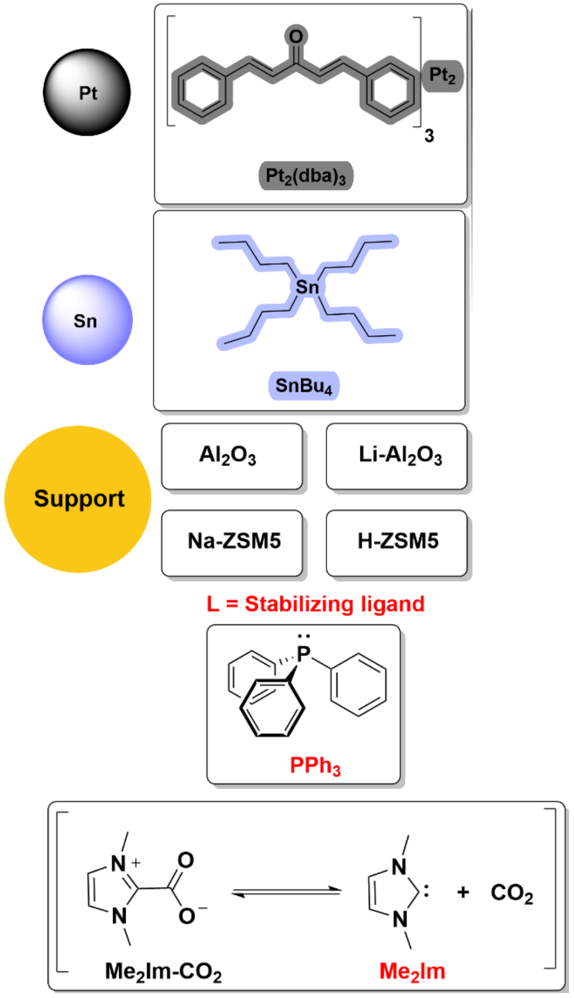
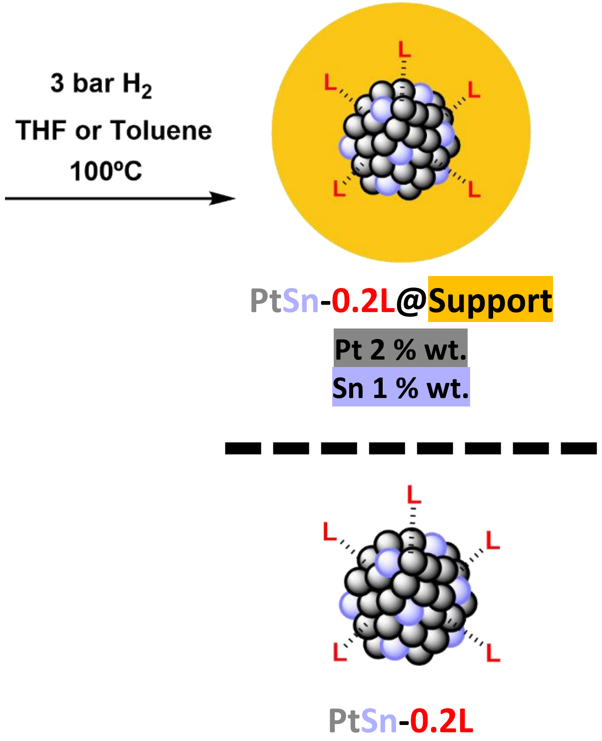
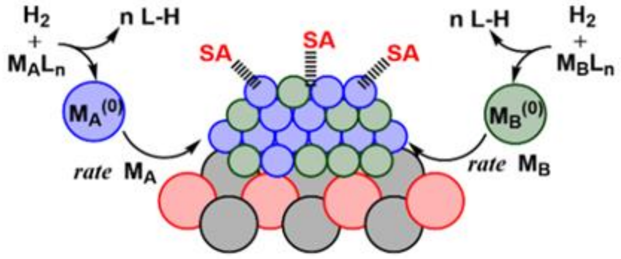
Nanocatalysts preparation: OPOA

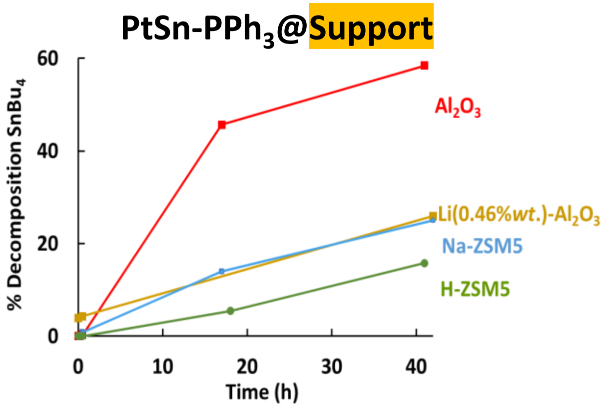


· Organometallic precursors
· Mild conditions (T,P)
· Ligand control (SA)
· Tunable catalytic properties
· Control (small) size and shape
· Addition of support





· In-situ monitoring (GC-TCD)



FUNDACIÓ EURECAT. *Alkane dehydrogenation nanocatalyst and process for its preparation*. Gil Jiménez, L.; Vicente Valverde, I.; Gual Gozalbo, A.; Godard, C.; Claver Cabrero, C. European patent application nº EP21382154.9. (2021).

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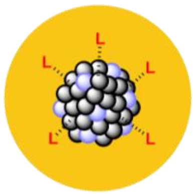
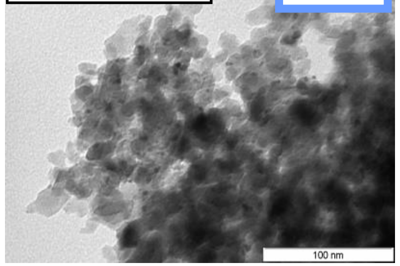
Nanocatalysts characterization: OPOA



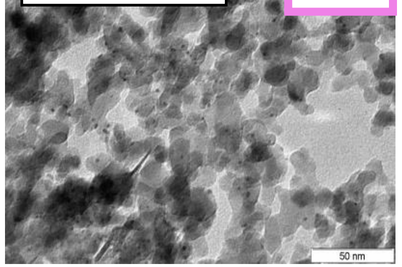
PtSn-0.2L@Support

1.6 ± 0.3 nm | PPh_3



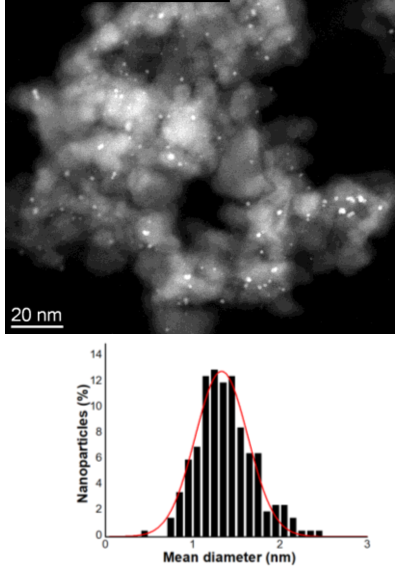
Effect of Ligand

1.6 ± 0.5 nm | NHC



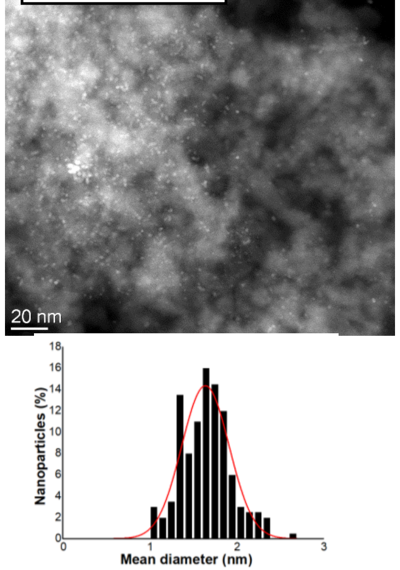
Al_2O_3

1.6 ± 0.3 nm



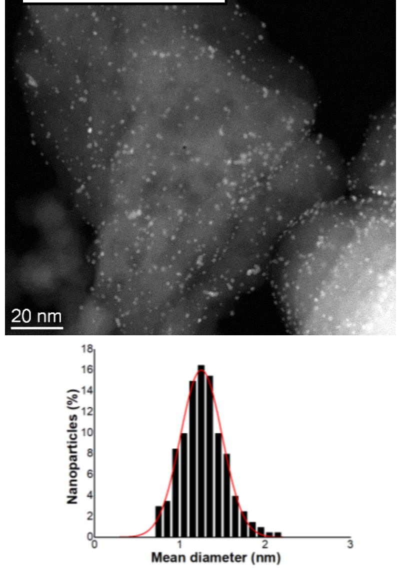
$Li\text{-}Al_2O_3$

1.3 ± 0.3 nm



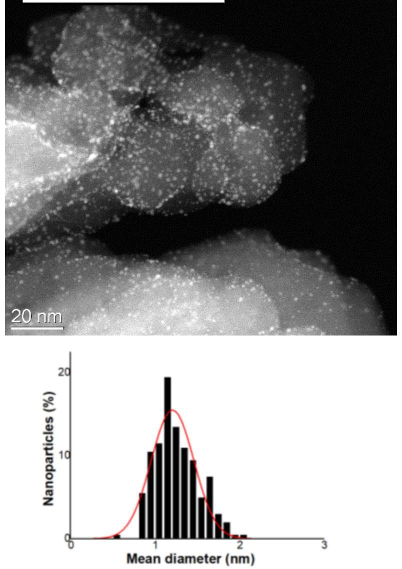
H-ZSM5

1.3 ± 0.2 nm



Na-ZSM5

1.2 ± 0.3 nm



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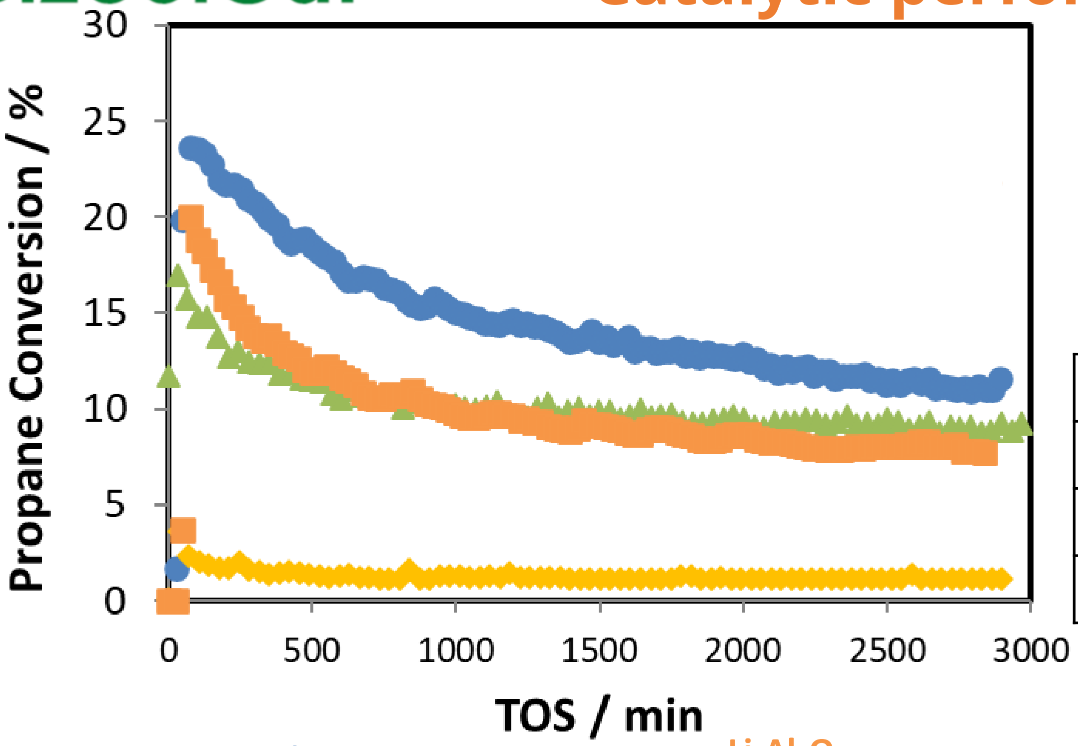
Catalytic performance PDH: OPOA

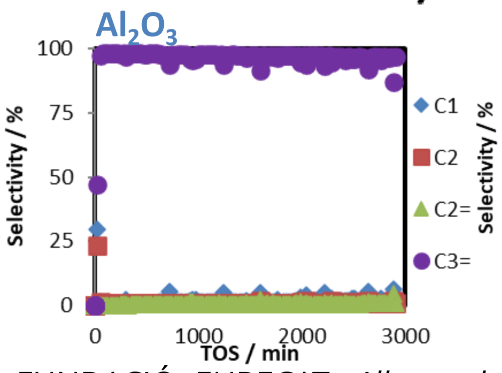


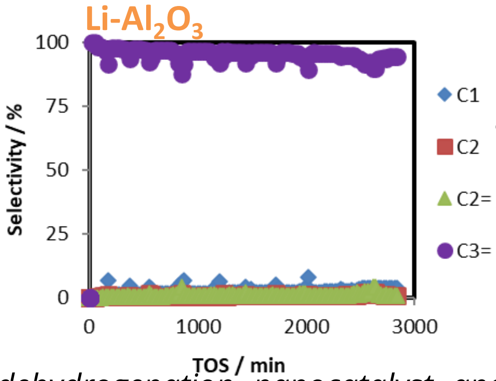
ΔH^{o} = 124 kJ.mol^{-1}

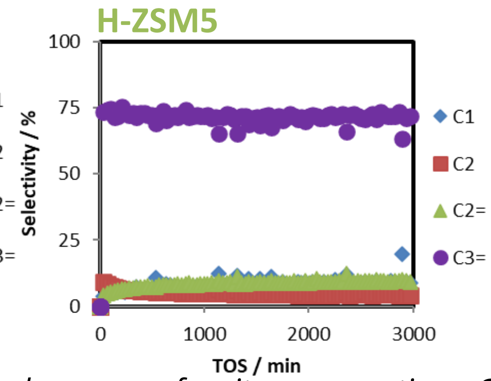
	ICP Sn/Pt
PtSn-PPh$_3$@Al$_2$O$_3$	1.04
PtSn-PPh$_3$@Li-Al$_2$O$_3$	0.66
PtSn-PPh$_3$@H-ZSM5	0.81
PtSn-PPh$_3$@NaZSM5	0.48

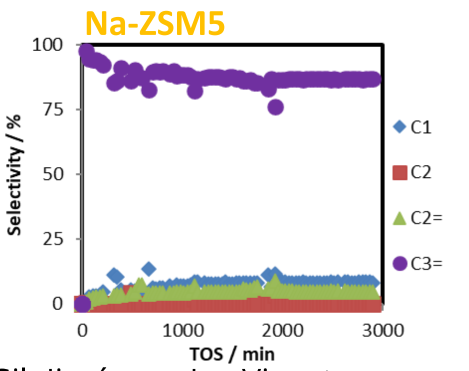
PRETREATMENT: 550 ºC reduction H_2 +purge Ar
CATALYSIS: 530 ºC total flow 25 mL/min P= 1 bar
21 Ar / 1 H_2 /3 C_3H_8 (mL/min).

Oleflex®:
T= 525-705 °C
P= 1 to 3 bar
Conv. of 22-70 %, Sel. 85%
Cycle time: 15-30 min









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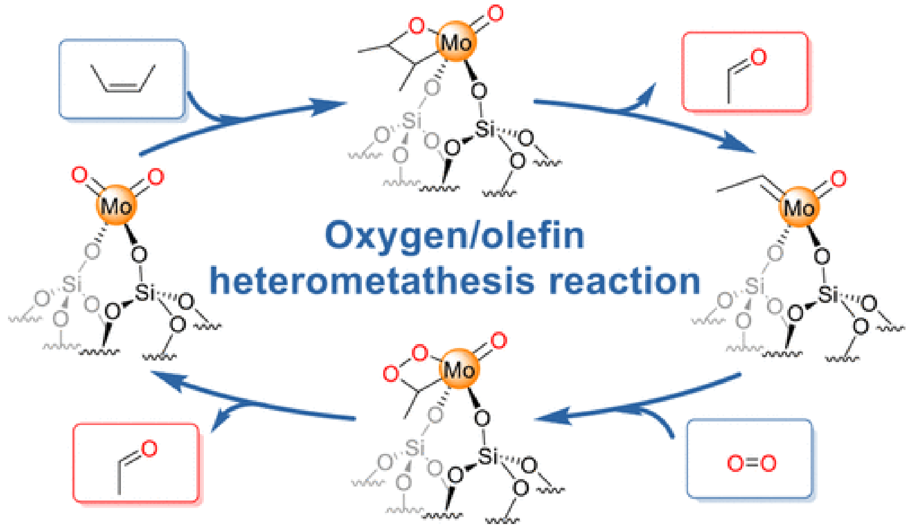
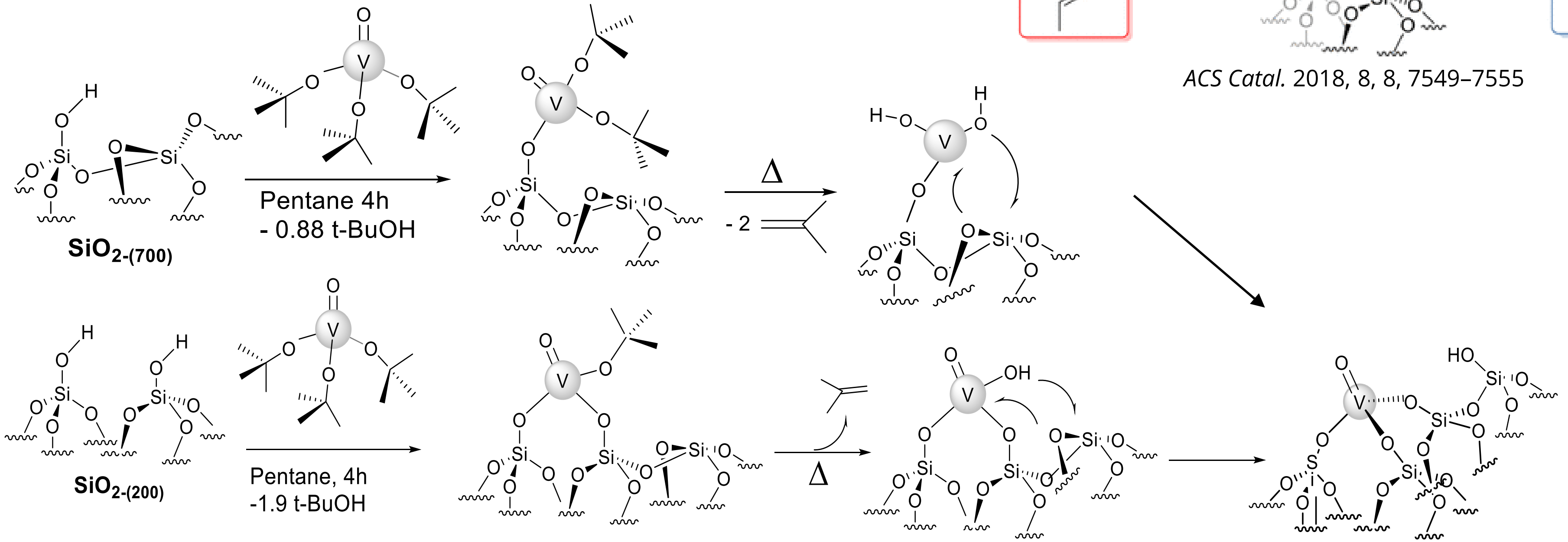
Nanocatalysts preparation: SOMC

- Use of vanadium complex bearing tert-butoxide ligand
- Combining SOMC and structuration of the support under thermal treatment



ACS Catal. 2018, 8, 8, 7549–7555



CP2M Catalyse, Polymérisation Procédés & Matériaux

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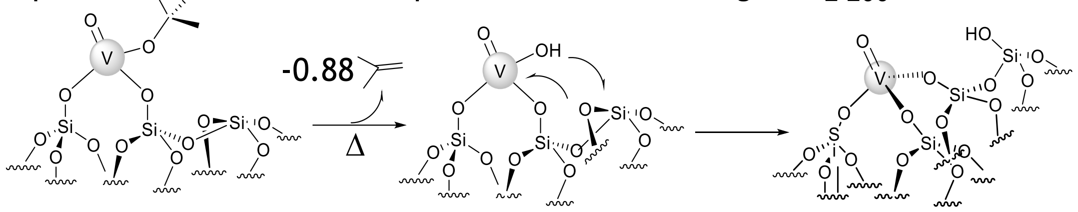
Nanocatalysts characterization: SOMC

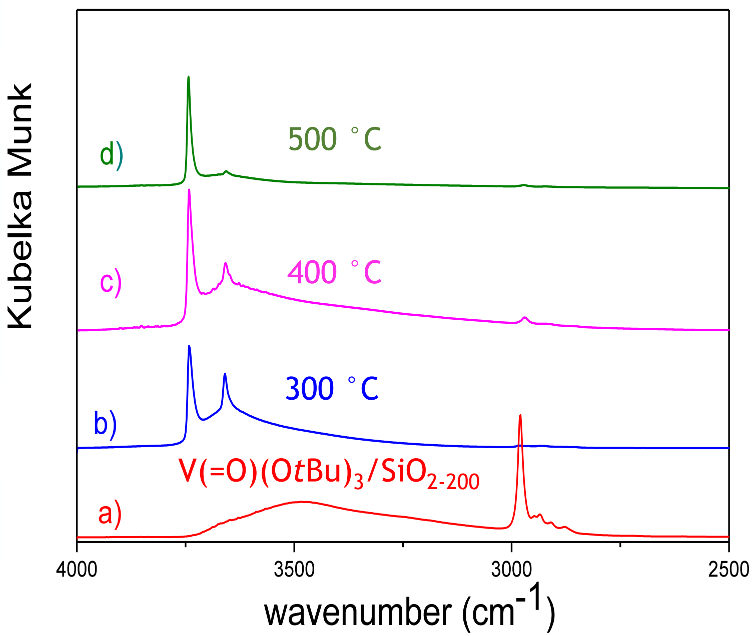
Tripodal oxo vanadium species V(=O)(O*t*Bu)$_3$/SiO$_{2\text{-}200}$



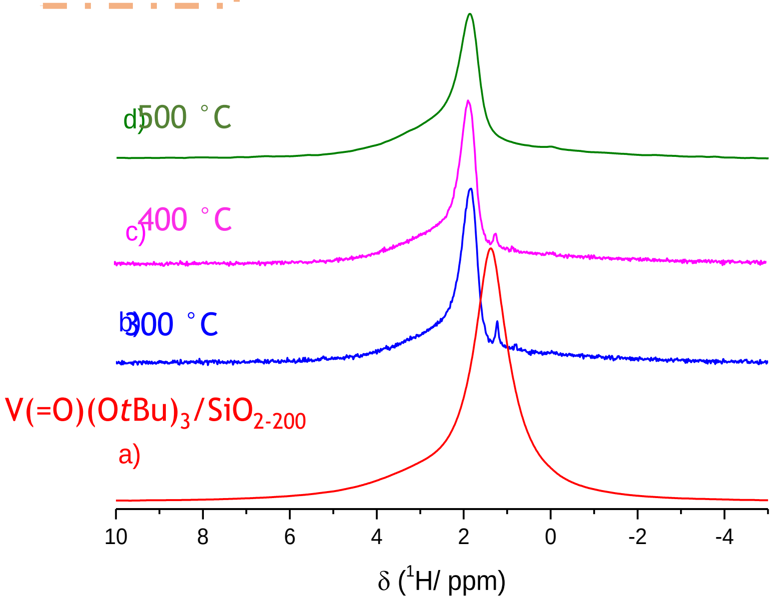
DRIFT: *Total disappearance of the alkyl vibrational bands
* Reappearance of isolated silanol groups at 3747 cm^{-1} and a new band at 3660 cm^{-1} attributed to n$_{VO\text{-}H}$

NMR: ^{1}H * Reappearance of isolated silanol groups at 1.8 ppm
^{51}V * Signal at -670 ppm attributed to [(≡SiO)$_3$V(=O)] isolated vanadium surface species

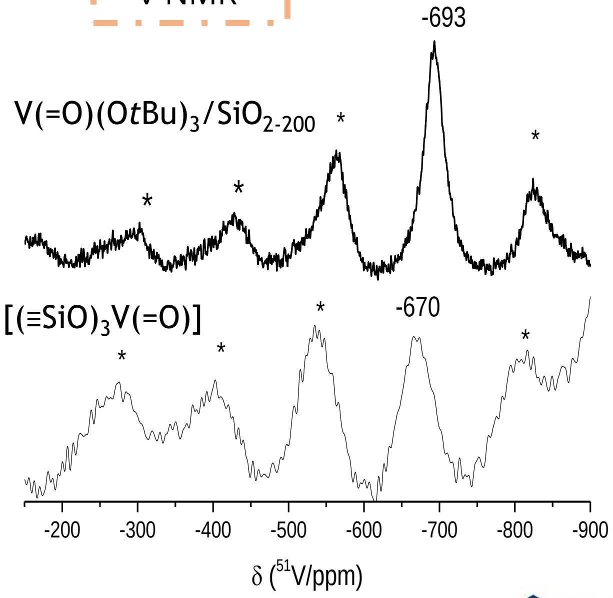
DRIFT spectroscopy



^{1}H NMR



^{51}V NMR



The thermal treatment of bipodal [(≡SiO)$_2$V(=O)(O*t*Bu)] leads to a tripodal oxo vanadium [(≡SiO)$_3$V(=O)]

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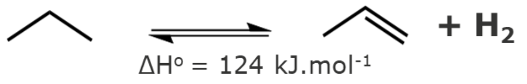
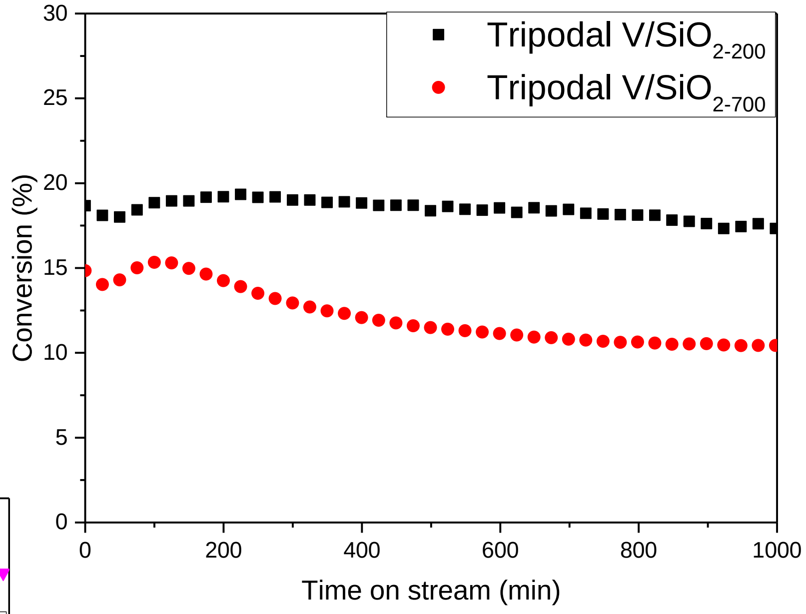
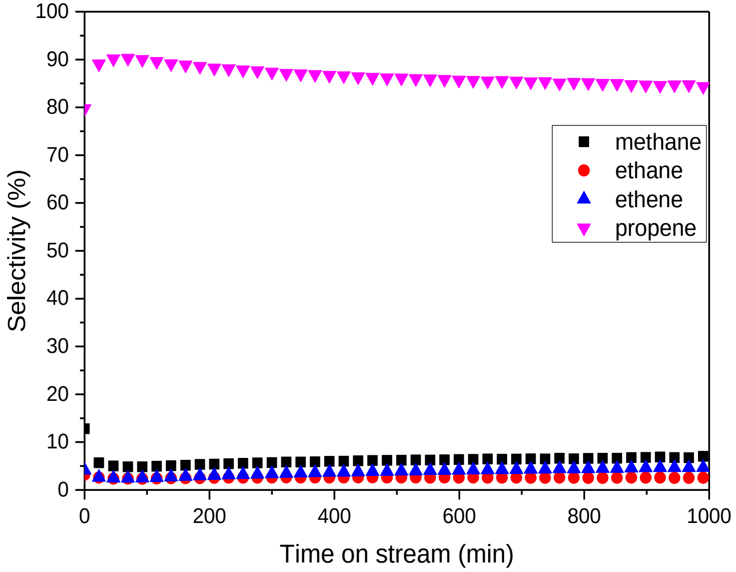
Catalytic performance PDH: SOMC

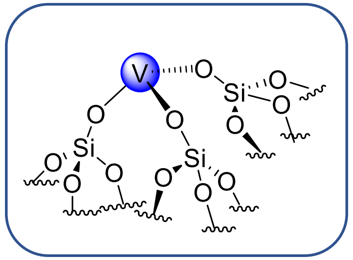
T= 540°C, P = 1 bar, 20% C_3H_8 in Ar,
Total flow = 5 mL.min⁻¹



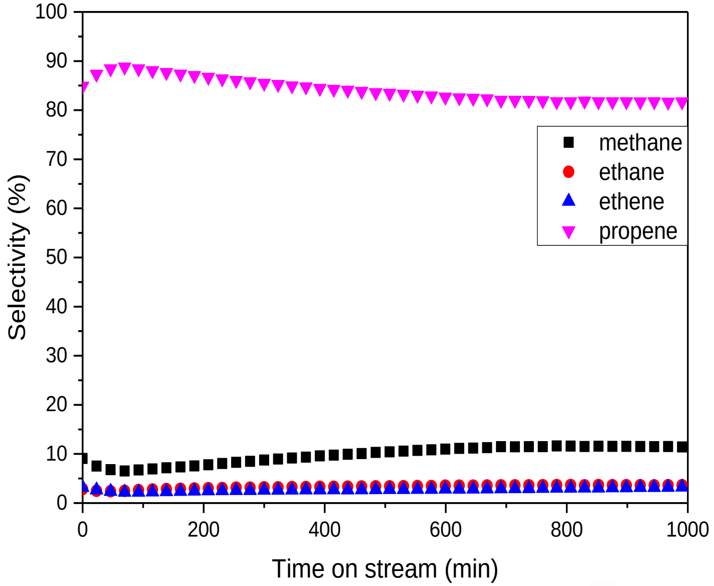


Tripodal V/$SiO_{2\text{-}200}$



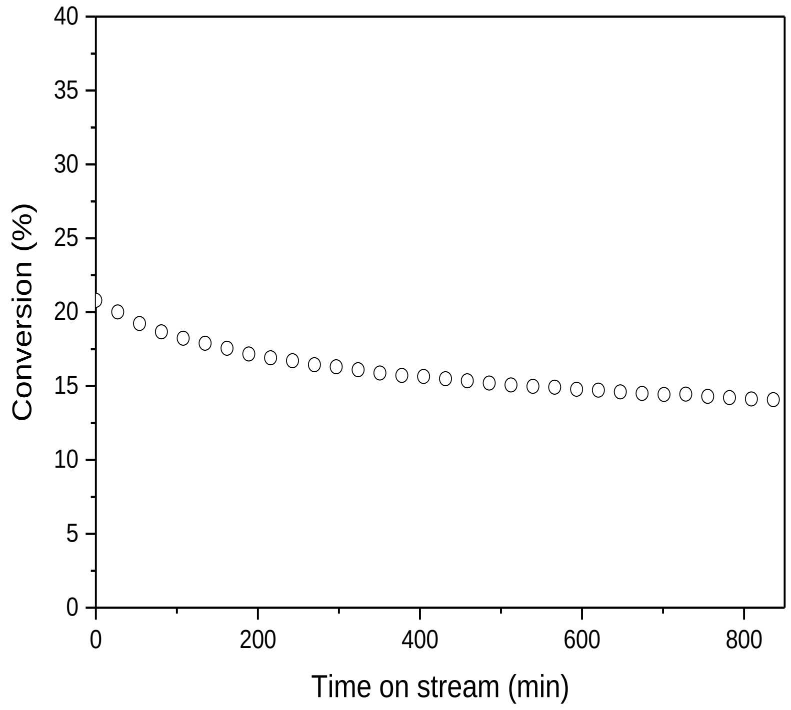


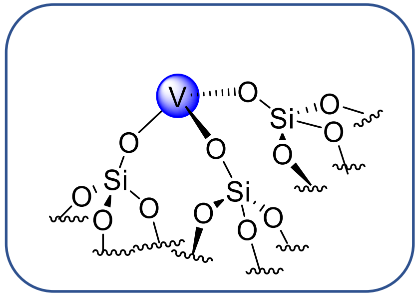
Tripodal V/$SiO_{2\text{-}700}$

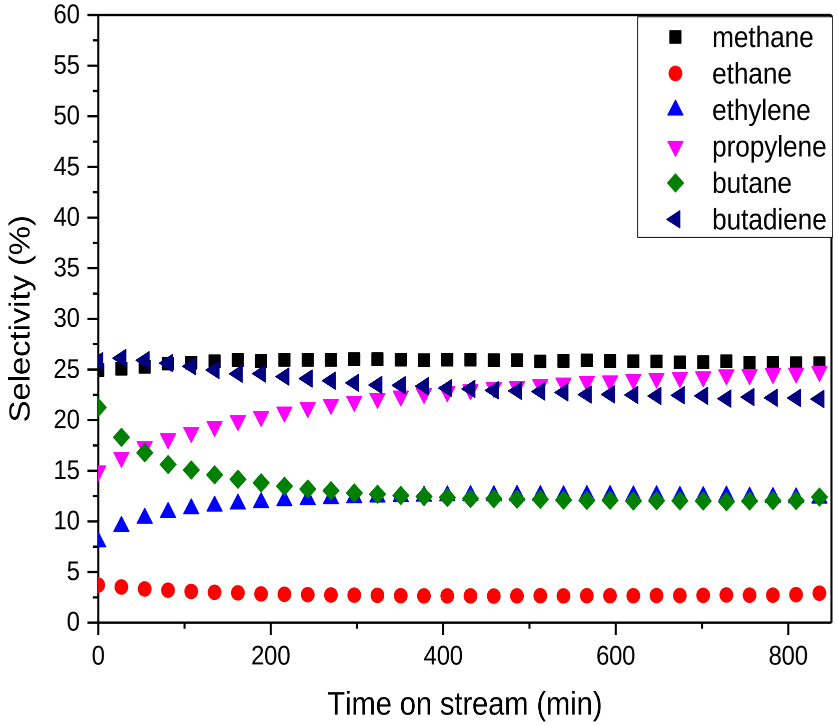


Catalytic performance BDH: SOMC

P = 1 bar, T= 540 °C, 20% 2-butenes in argon, Total flow = 5 mL.min^{-1} (Ar/2-C_4= = 4/1)

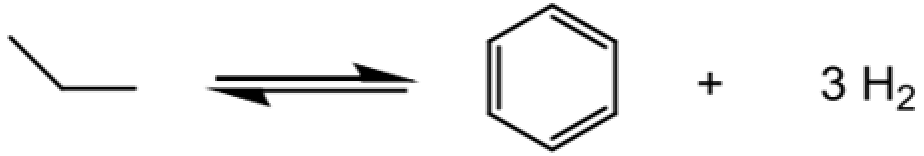


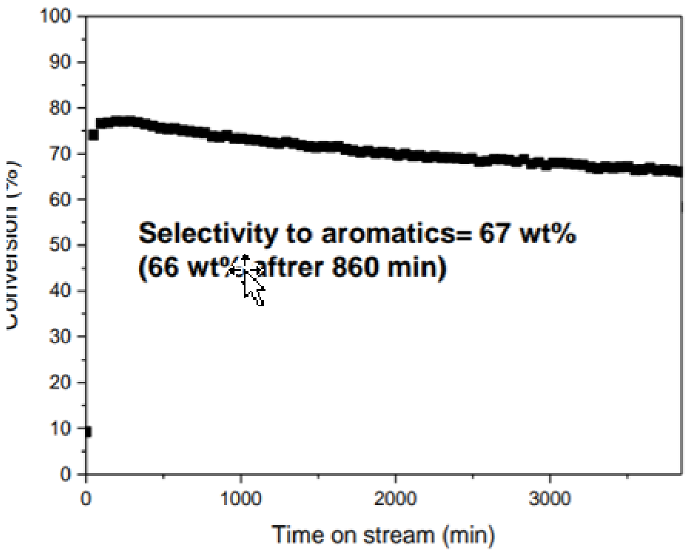


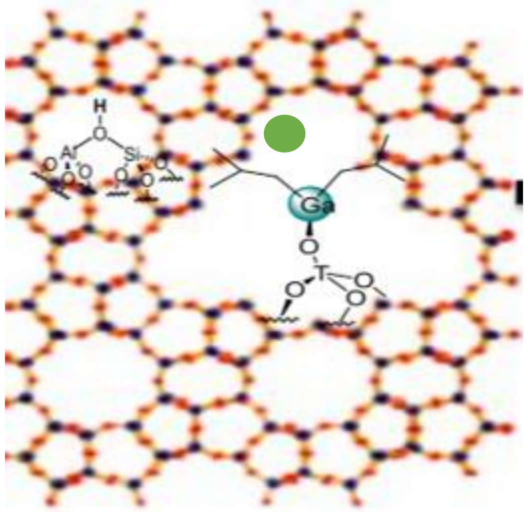


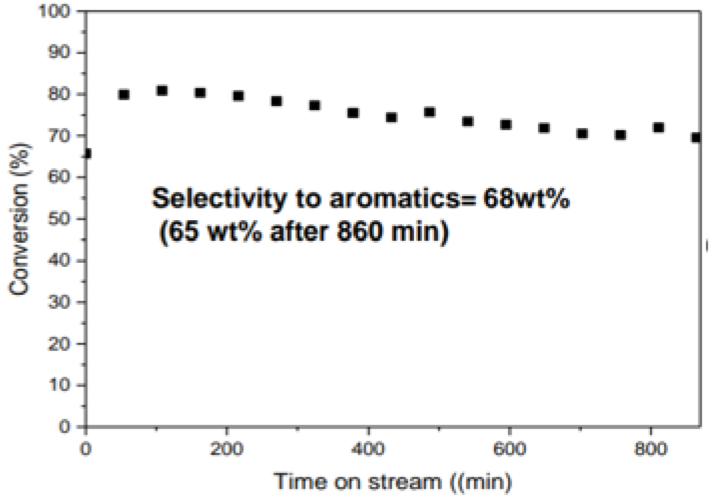
Catalytic performance PAr: SOMC

540 ºC total flow 10 mL/min.
P= 1 bar, 2,5% C_3H_8 in Ar









Cyclar®
T= 550-650 °C
Sel. of 63%

Conclusions

- New beyond of the SotA catalysts were designed and developed for three different processes: PDH, BDH, PAr, obtaining high conversion, selectivity and stability results.

- For OPOA Pt-Sn/Al_2O_3 NPs catalysts:
  - In the synthesis of PtSn PDH catalyst by one-Pot-Organometallic Approach, the decomposition of Sn precursor is highly affected by both support or ligand.
  - In PDH experiments, Sn content is directly related to propane conversion while selectivity is affected by the support.

- For SOMC single site catalysts:
  - The thermal treatment of monopodal bipodal vanadium species leads to a tripodal oxo vanadium $[(\equiv SiO)_3V^V(=O)$.
  - The activity and selectivity of tripodal V obtained on SiO_{2-200} seem better than those obtained on SiO_{2-700} due to the difference in the local structure of the tripodal V on silica.

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THANK YOU

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 814671

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Journal of Catalysis
Volume 126, Issue 1, November 1990, Pages 267-278

Ga_2O_3/HZSM-5 propane aromatization catalysts: Formation of active centers via solid-state reaction

Geoffrey L. Price *, Vladislav Kanazirev †

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Abstract

An active and very selective catalyst for propane conversion to aromatics near atmospheric pressure and 750–850 K is formed by ball-milling 2–10 wt% Ga as Ga_2O_3 with HZSM-5 followed by hydrogen reduction at about 850 K for 2 h. Microbalance TPR experiments and X-ray diffraction studies along with catalytic testing have helped establish that the intimate physical mixture of Ga_2O_3 with HZSM-5, the acidity of the zeolite, and the hydrogen reduction are all necessary to generate the highly active form of the catalyst. The active species is probably Ga(I) as a zeolitic cation and is not incorporated in the zeolite lattice.

Petrochemicals produced from BTX [edit]

There are a very large number of petrochemicals produced from the BTX aromatics. The following diagram shows the chains lea from the BTX components to some of the petrochemicals that can be produced from those components:[2]

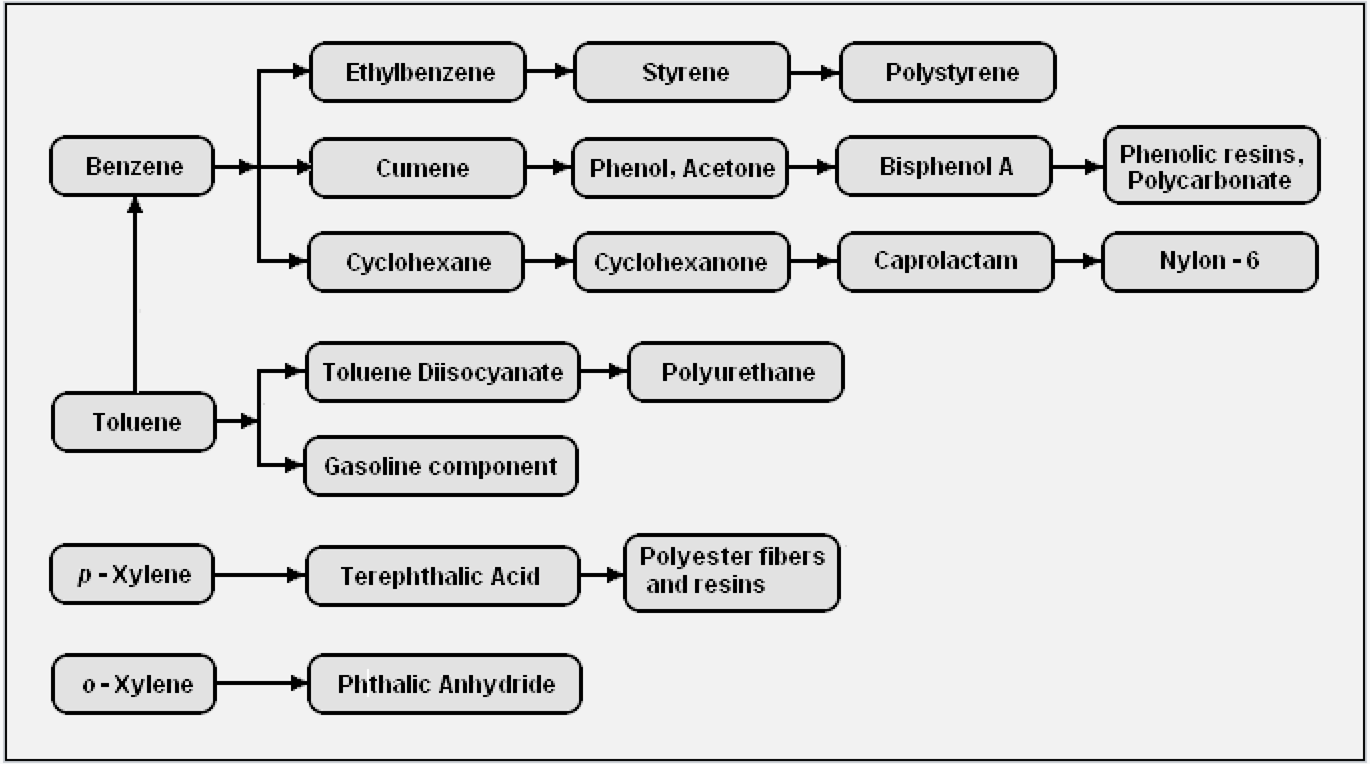


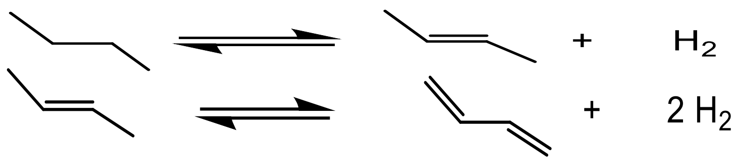
Diagram of the chain of petrochemicals derived from the BTX aromatics.

Non-oxidative alkane dehydrogenation on supported metal oxides: Industrial plants

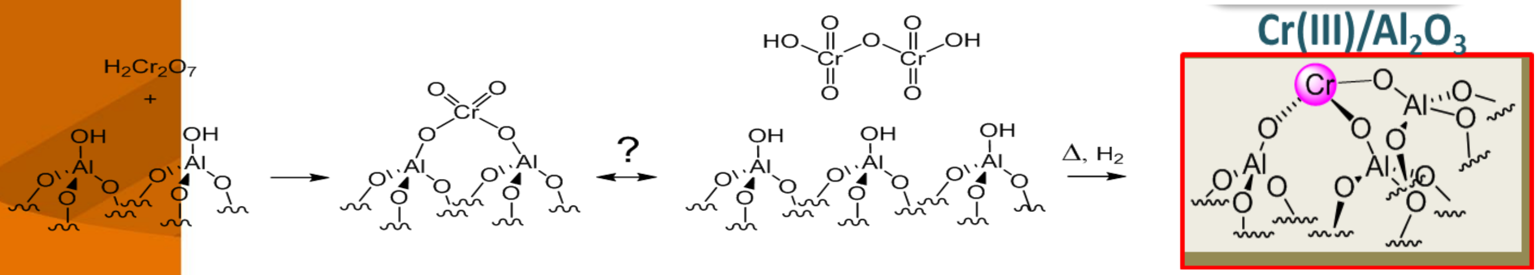
Catofin®: T= 590-650 °C (high temperature)
P= 0.2 and 0.5 bar
Conv. of 48-65 %, Sel. of 82 %
Cycle time: 15-30 min

Catalyst : $CrOx/Al_2O_3$

Catadiene® : T= 600-620 °C (high temperature)
P= 0.2 and 0.4 bar of C4
Conv. of 30-40 %, Sel. of 60% butadiene
(2 steps are required)



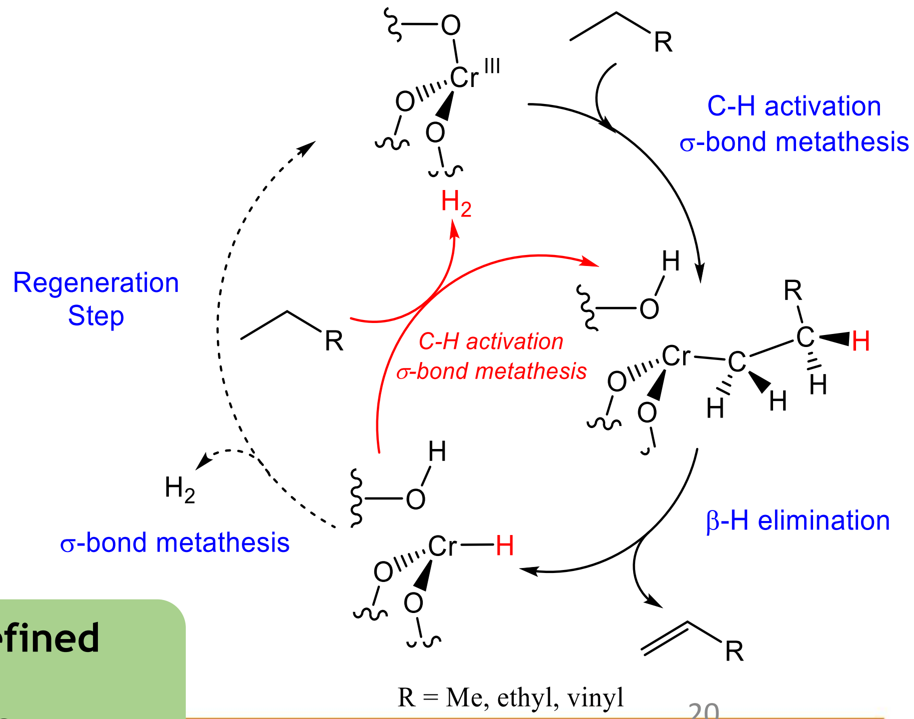
Catofin and Catadiene processes (ABB Lummus)



- High loading of Cr (18-20 wt%) on modified alumina by classical methods
- Mixture of monomeric, dimeric and oligomeric species on the surface
- Low concentration of active sites on the surface
- Regeneration every 15-30 min
- Incorporation of Cr in the framework of alumina leading to a loss of activity

× Chromium toxicity
× High operating temperature
× Fast deactivation
× Lack of characterization

Proposed mechanism for metal oxides



Eco-friendly, low-cost, stable and well-defined catalysts are required.
Development of new catalysts based on V, Ga, Zn…

BIZEOLCAT Introduction: Benchmark PDH Technologies

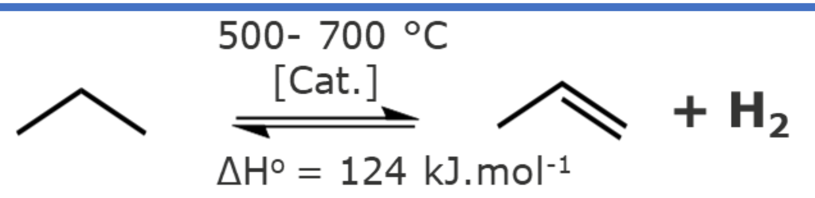
Support: Al_2O_3 and modified Al_2O_3 based materials.
Current limitation: Thermodynamic conversion, selectivity and stability.

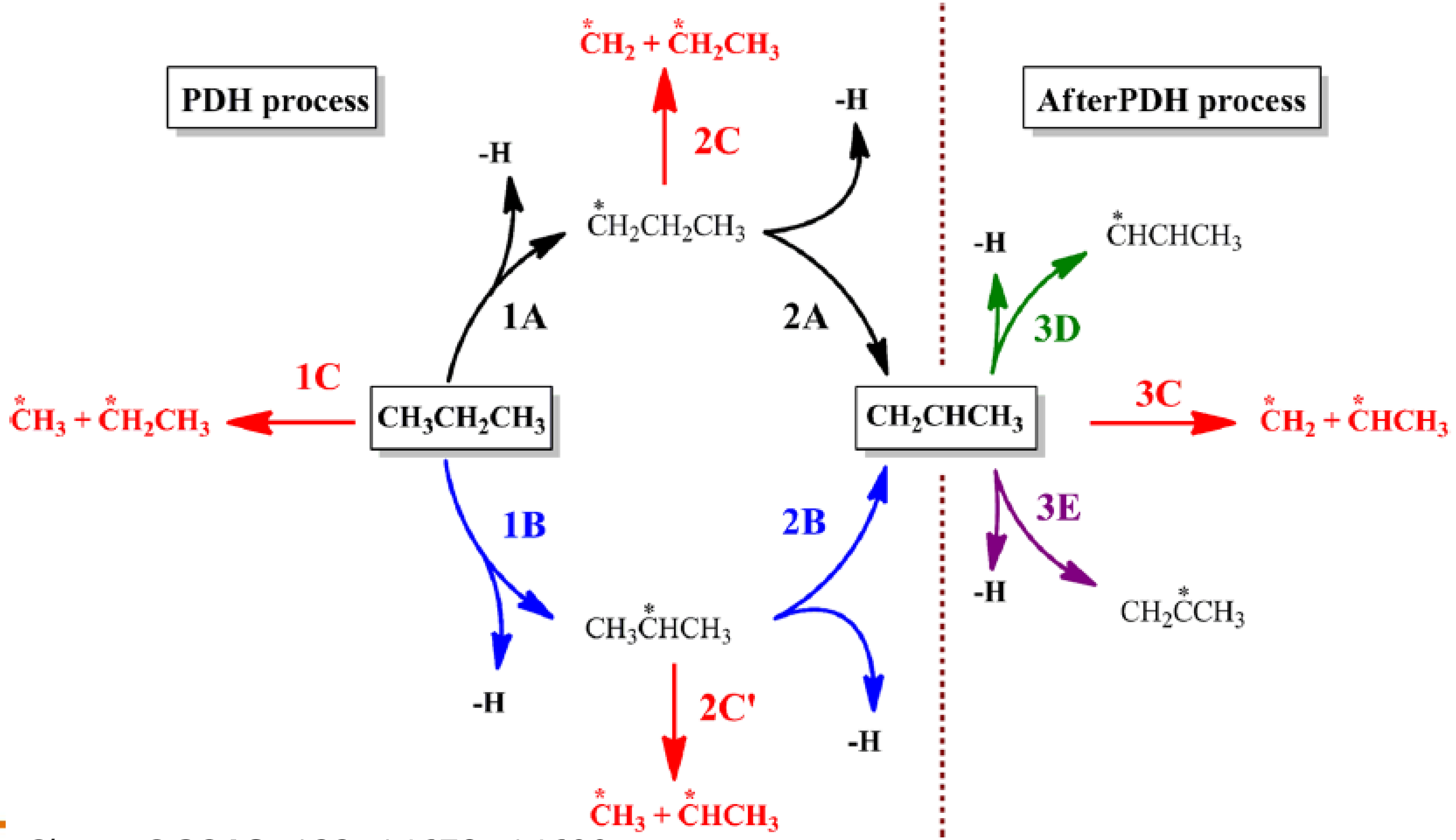
Technology	Oleflex	PDH	STAR	FCDh
Developer	UOP	Linde-BASF	Phillips	Dow Chemical Company
Time	1990	1995	1999	2016
Reactor	Moving bed	Tubular fixed bed	Tubular fixed bed	Up-flow fluidized bed
Catalyst	K(Na)-Pt-Sn/Al_2O_3	Pt-Sn/ZrO_2	Pt-Sn/$ZnAl_2O$ $CaO-Al_2O_3$	Pt-Ga-K/Si-Al_2O_3
T/°C	525–705	550–650	480–620	~600
P/bar	1–3	>1	5–6	1
WHSV/h^{-1}	4–13	—	0.5–10	
Dilute gas	Cyclic H_2	None	Stream	N_2
Operating period	Continuous operation, 5–10 days	Reaction 6 h, regeneration 3 h	Reaction 6 h, regeneration 2 h	Continuous regeneration
Catalyst life/years	1–3	>2	>5	—
Conversion/%	30–40	40–45	~35	~45
Selectivity/%	85.5–88	95	80–90	~93

· Operates at high T (500-700 ºC)
· Difficult to control selectivity
· Metal sintering
· Coke formation
· Need of regeneration

S. Chen and co-workers, *Chem. Soc. Rev.*, **2021**,*50*, 3315-3354.
Z. Nawak and co-workers, Rev. Chem. Eng., **2015**, *31*, *5*, 413–436

BIZEOLCAT Introduction: PDH Mechanism

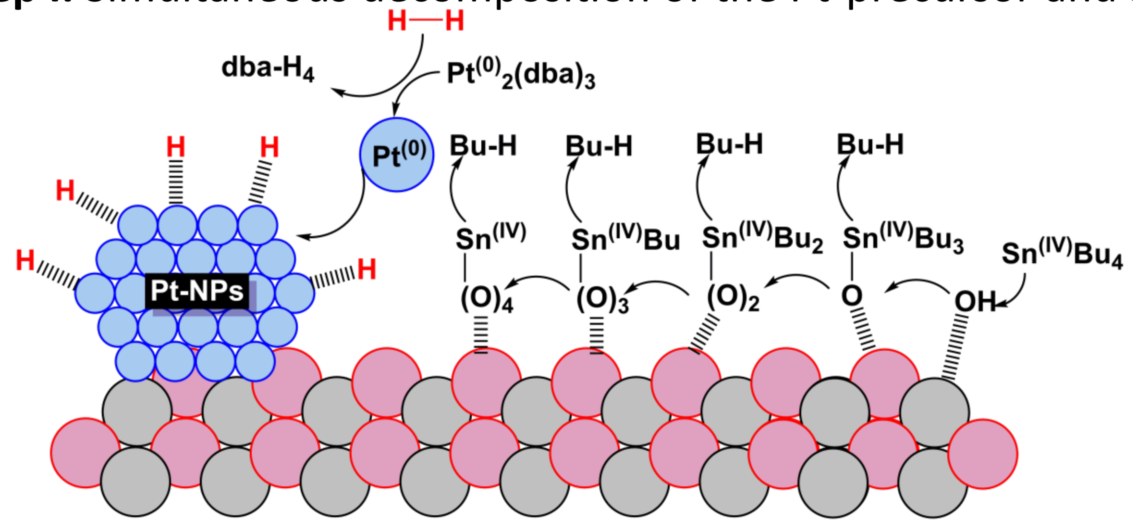




J. Phys. Chem. C **2018**, 122, 14678−14690

BIZEOLCAT:
Nanoparticle Formation Mechanism

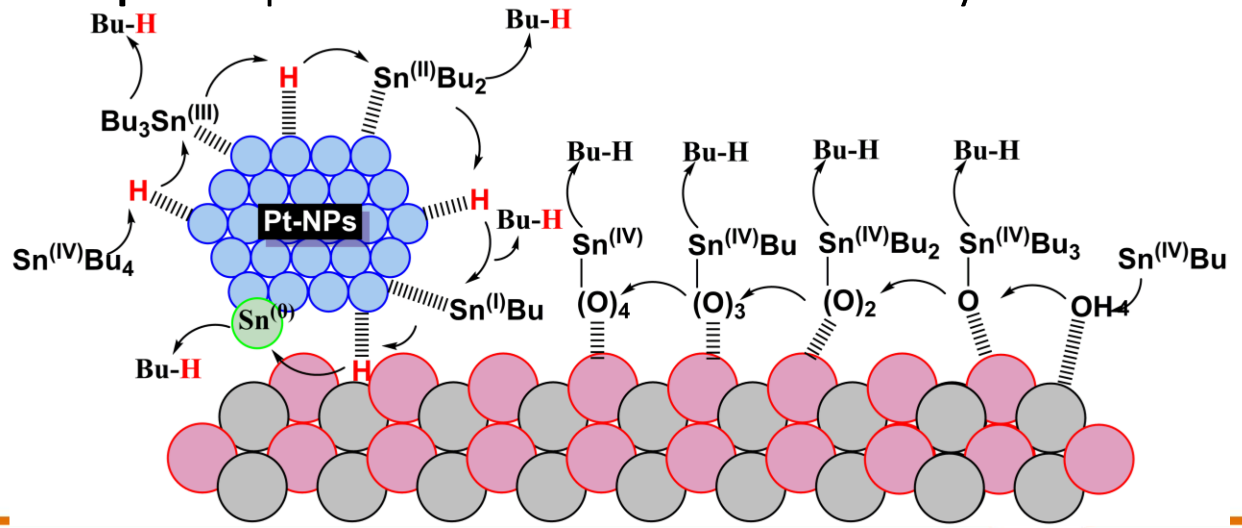
Step I. Simultaneous decomposition of the Pt-precursor and Sn-precursor.



Hypothesis, Ligand Effect (I):

- Modulated the reactivity of the Sn-precursor with the amphoteric OH.
- Stabilized small and well dispersed Pt-NPs.

Step II. Sn-precursor reaction with the Pt-NP hydrides.

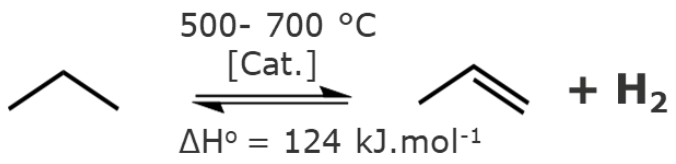


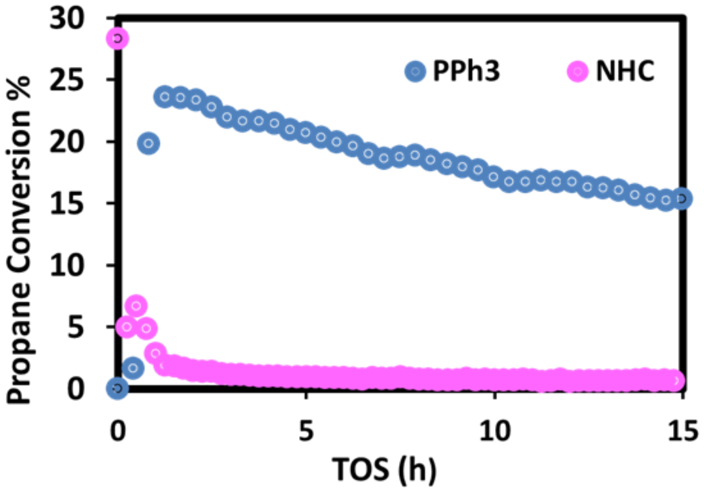
Hypothesis, Ligand Effect (II):

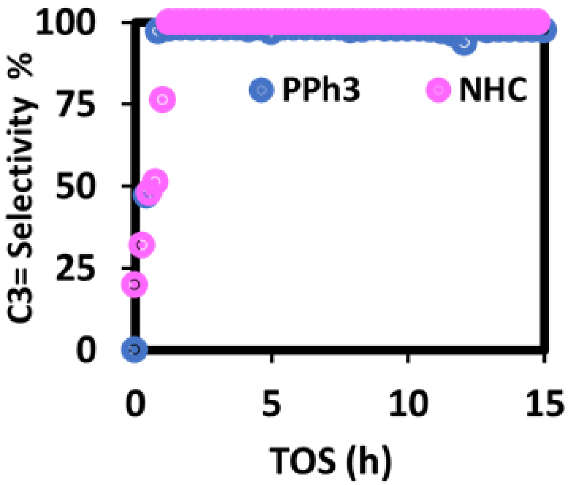
- Ligand coordinated in the Pt-NPs modulated the reactivity with Sn-precursor.

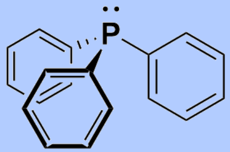
BIZEOLCAT: Nanocatalysts Evaluation

Effect of LIGAND

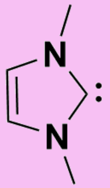








PPh_3

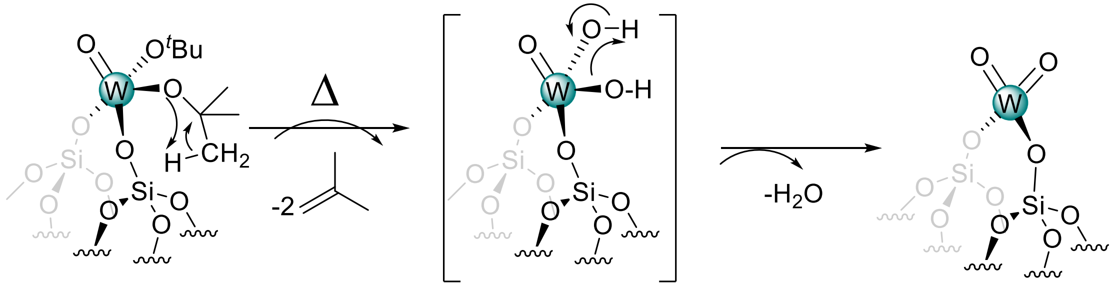


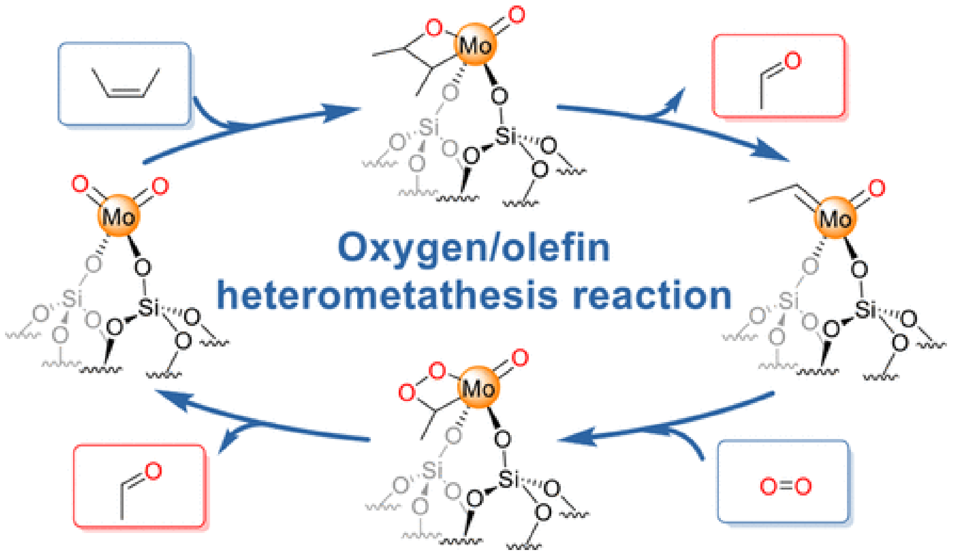
NHC

	ICP Sn/Pt
PtSn-PPh_3@Al_2O_3	1.04
PtSn-NHC@Al_2O_3	0.29

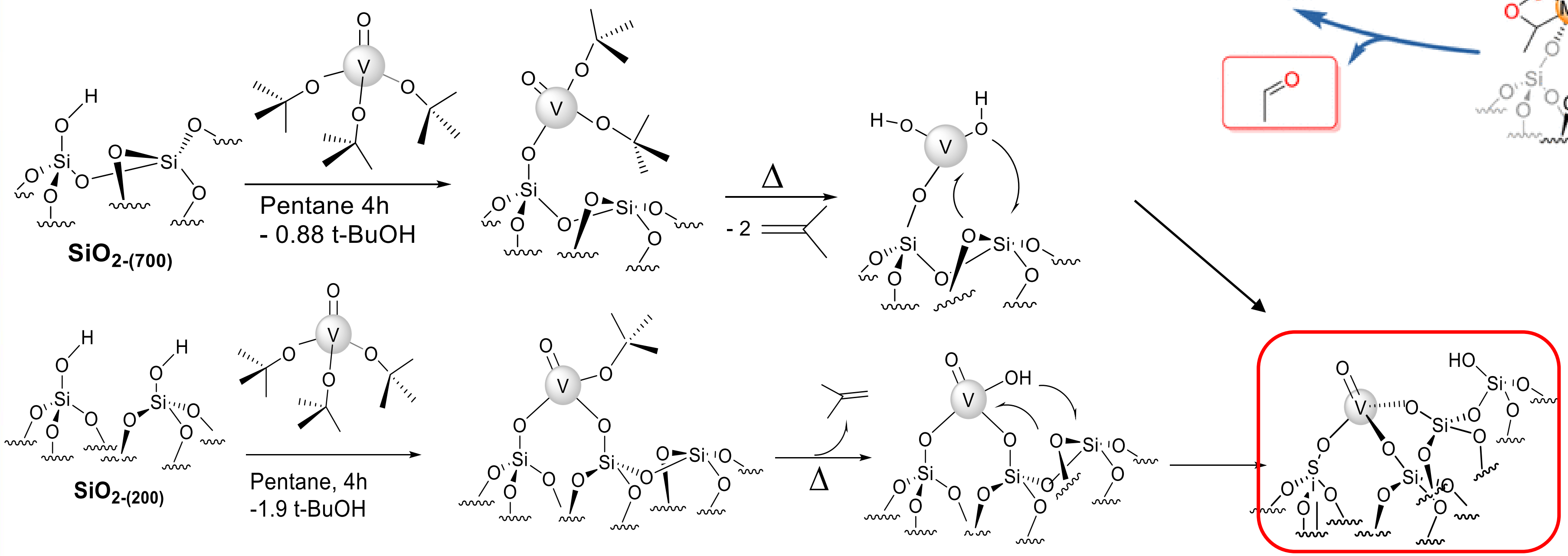
FUNDACIÓ EURECAT. *Alkane dehydrogenation nanocatalyst and process for its preparation*. Gil Jiménez, L.; Vicente Valverde, I.; Gual Gozalbo, A.; Godard, C.; Claver Cabrero, C. European patent application nº EP21382154.9. (2021).

Nanocatalysts preparation: SOMC





Application of this strategy to vanadium supported catalysts:

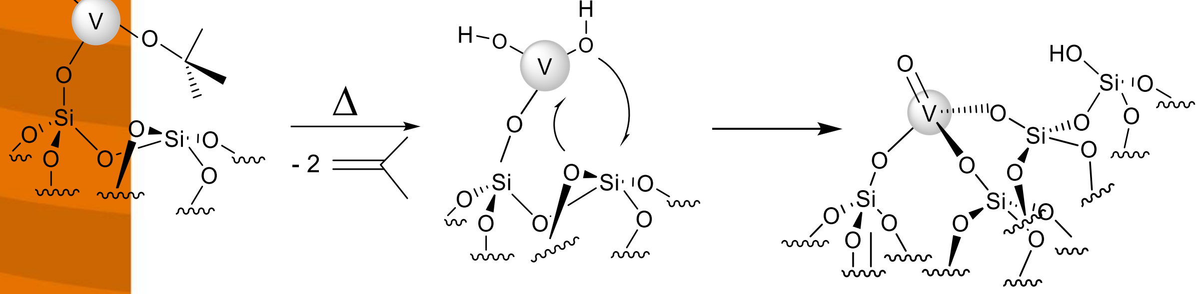


ACS Catal. 2018, 8, 8, 7549–7555

- Use of vanadium c
- Combining SOMC a

New synthetic m

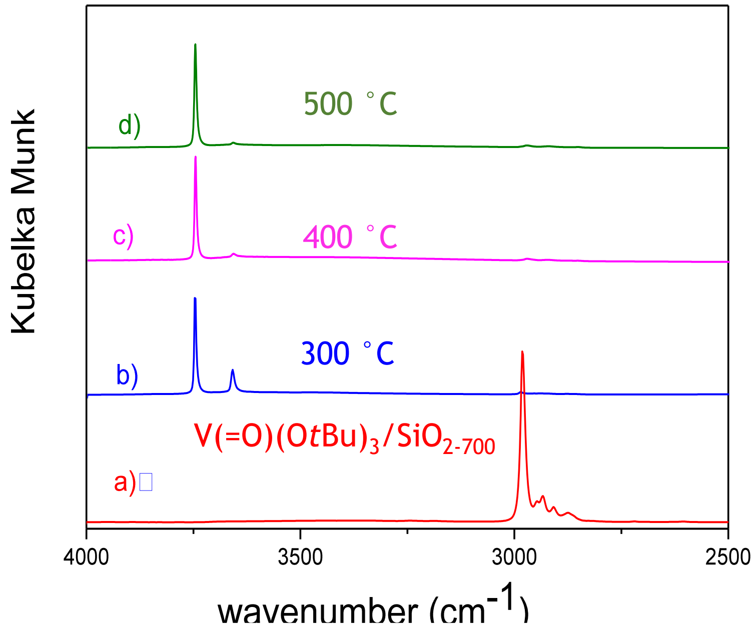
Characterization of tripodal oxo vanadium species $V(=O)(OtBu)_3/SiO_{2\text{-}700}$



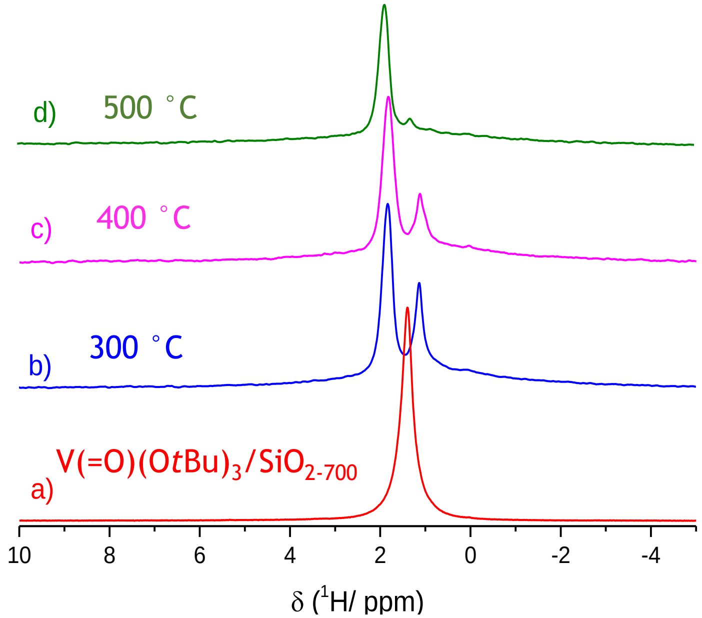
DRIFT: *Total disappearance of the alkyl vibrational bands
* Reappearance of isolated silanol groups at 3747 cm^{-1} and a new band at 3660 cm^{-1} attributed to $\nu_{VO\text{-}H}$

NMR: ^{1}H * Reappearance of isolated silanol groups at 1.8 ppm
^{51}V * Signal at -670 ppm attributed to $[(\equiv SiO)_3V(=O)]$ isolated vanadium surface species

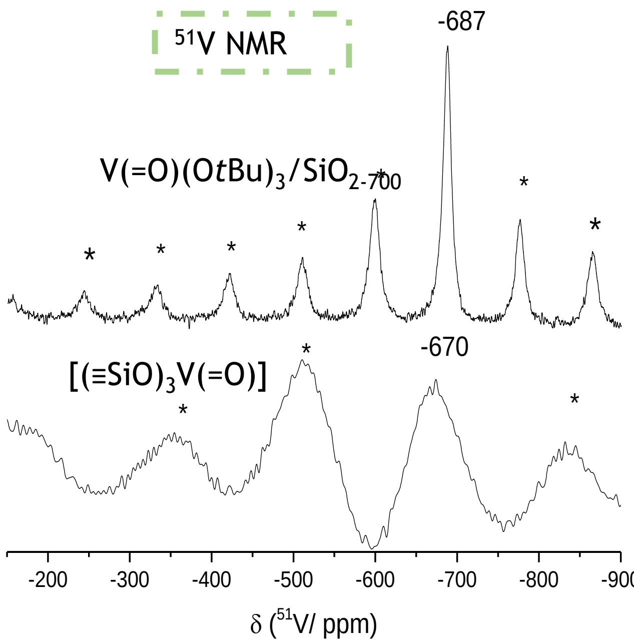
DRIFT spectroscopy



^{1}H NMR



^{51}V NMR

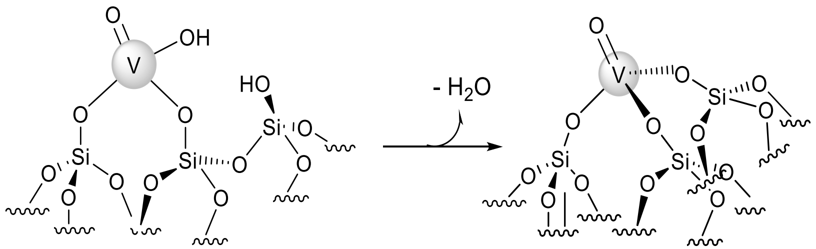


The thermal treatment of monopodal $[(\equiv SiO)V(=O)(OtBu)_2]$ leads to a tripodal oxo vanadium $[(\equiv SiO)_3V(=O)]$

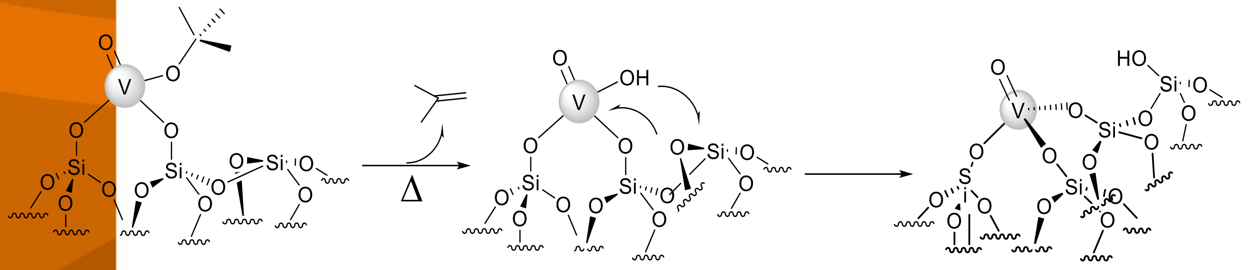
Proposed mechanism for the formation of tripodal V oxo

The disappearance of the vibration band V-OH during thermal treatment:

1. Partial condensation of V-OH with remaining silanols, leading to the formation of water and V-OSi bonds and decrease in the SiOH band vibration

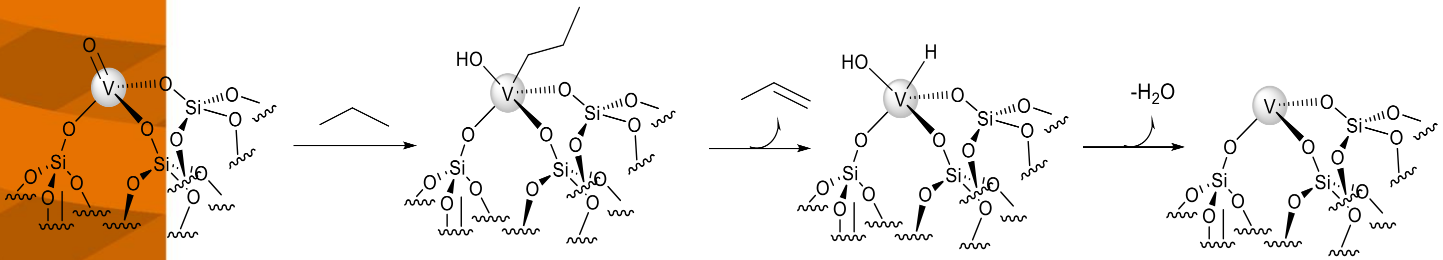


(2a)



2. Release of isobutene leading to a V-OH fragment followed by ring openning of Si-O-Si, leading to the formation oxo vanadium tripodal species and regeneration of SiOH

Reduction of V^{5+} into V^{3+} after activation of propane and release of water



- Hydrogen abstraction of C_3H_8 occurs on V=O ligand of [(≡SiO)$_3$V(=O)]
- β-H elimination of the V coordinated propyl ligand, leading to the formation of V hydrido hydroxyl species and release of one propylene.
- Reductive elimination of H_2O leads to the formation of the active tripodal species, [(≡SiO)$_3$V$^{(III)}$]

These resutls are in agreement with the reported literature on the reduction of V^{5+} into V^{3+}