Финансирано от
Европейския съюз
NextGenerationEU

SUMMIT
SOFIA UNIVERSITY
MARKING MOMENTUM
FOR INNOVATION AND
TECHNOLOGICAL TRANSFER

Национален план за
възстановяване и устойчивост
НА РЕПУБЛИКА БЪЛГАРИЯ

Zeolitic materials for new applications

Valentin Valtchev

До говор BG-RRP-2.004-0008 за финанси ране на проект „СОФИЙСКИ УНИВЕРСИТЕТ – МАРКЕР ЗА ИНО ВАЦИИ И ТЕХН ОЛОГИЧЕН Т РАНСФЕР (S UMMIT)“ по ст ълб 2 „Създаване на мрежа о т изследо вателски висши училищ а“
в рамките на к о мпонент „Ино вативна България“ о т Национален план за възс тановя ване и ус тойчивост к ъм прог рам ата за ускоря ване на икон о мическ о то в ъзс тановя ване и т рансфо рмация чрез н аука и ино вации

Финансирано от Европейския съюз
NextGenerationEU

SUMMIT
SOFIA UNIVERSITY MARKING MOMENTUM FOR INNOVATION AND TECHNOLOGICAL TRANSFER

СОФИЙСКИ УНИВЕРСИТЕТ -
МАРКЕР ЗА ИНОВАЦИИ И ТЕХНОЛОГИЧЕН ТРАНСФЕР

Национален план за възстановяване и устойчивост
НА РЕПУБЛИКА БЪЛГАРИЯ

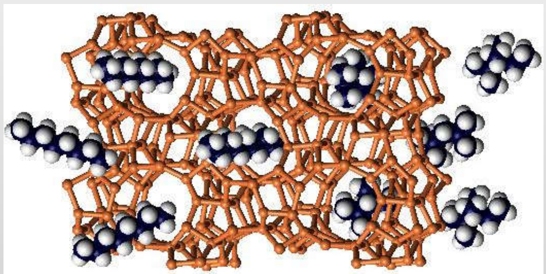
Defintion: *Zeolites are crystalline aluminosilicates, composed of TO_4 tetrahedra (T = Si, Al) with O atoms connecting neighbouring tetrahedral, that contain pores and cavities of molecular dimensions (Breck, 1974).*

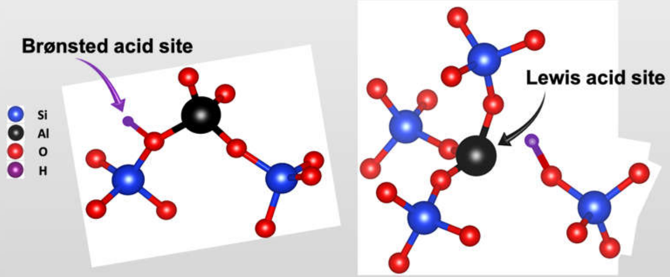
Properties

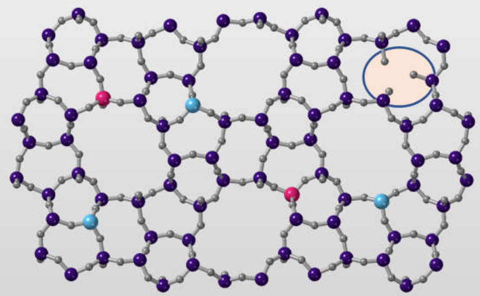
- Tunable acidity
- High surface area
- High thermal stability
- High chemical stability
- Well-defined micro-pore structure
- Shape-selectivity

Applications

- Heterogeneous catalysts in oil refining, petrochemical industry, fine chemicals
- Molecular sieves
- Separation of toxic gases and radioactive isotopes
- Environmental applications



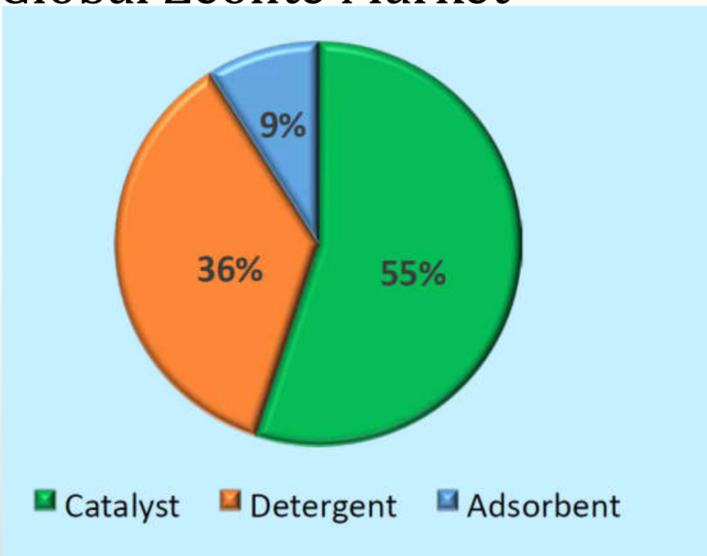


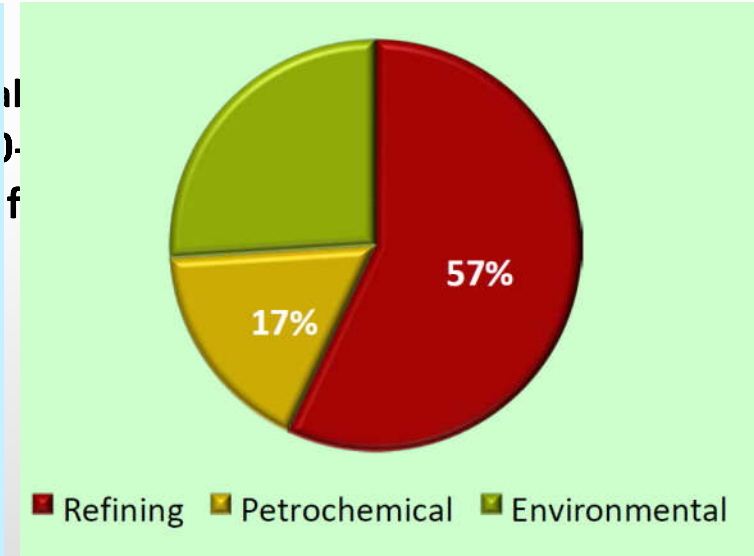


Договор BG-RRP-2.004-0008 за финансиране на проект „СОФИЙСКИ УНИВЕРСИТЕТ – МАРКЕР ЗА ИНОВАЦИИ И ТЕХНОЛОГИЧЕН ТРАНСФЕР (SUMMIT)“ по стълб 2 „Създаване на мрежа от изследователски висши училища“ в рамките на компонент „Иновативна България“ от Национален план за възстановяване и устойчивост към програмата за ускоряване на икономическото възстановяване и трансформация чрез наука и иновации

Michel BOUDART: *«Catalysis Blends Elegance and Relevance»*

Global Zeolite Market





Refining: FCC, Hydrocracking, Dewaxing Lubes/Distillates, Isomerization
Petrochemical: Xylenes (p-Xylene), Cumene, Ethyl Benzene
Environmental: Non-stationary and stationary

Финансирано от Европейския съюз
NextGenerationEU

СОФИЙСКИ УНИВЕРСИТЕТ -
МАРКЕР ЗА ИНОВАЦИИ И ТЕХНОЛОГИЧЕН ТРАНСФЕР

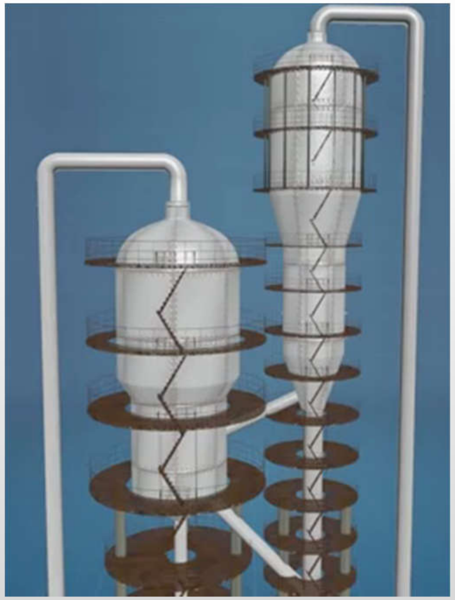
SUMMIT
SOFIA UNIVERSITY MARKING MOMENTUM FOR INNOVATION AND TECHNOLOGICAL TRANSFER

Национален план за възстановяване и устойчивост
НА РЕПУБЛИКА БЪЛГАРИЯ

Zeolites = Game Changer in FCC (60's)

Introduction of zeolites in FCC (1964) – a Disruptive Technology

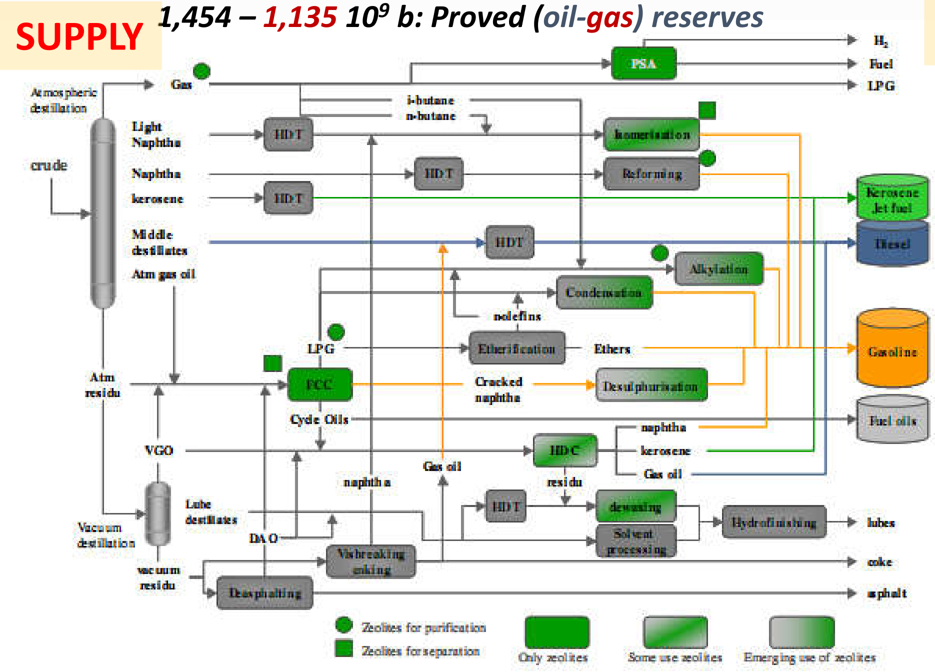
Fluid Catalytic Cracking (FCC)
a milestone in catalysis



~ 90 10^6 b/d

SUPPLY

1,454 – 1,135 10^9 b: Proved (oil-gas) reserves



DEMAND

- Changes in Transportation Fuels
  - Gasoline / Diesel shift
  - Higher quality, higher octane gasoline
- Chemicals (aromatics and light olefins) and high performance lubricants demand are up
- Changes in Feedstock
  - Shale Gas / Tight Oil
  - Heavy Oils
  - Renewables enter feed mix, but slowly
- Environmental Needs
  - Fuels regulations and emission standards
- Energy Efficiency

До говор BG-RRP-2.004-0008 за финанси ране на проект „СОФИЙСКИ УНИВЕРСИТЕТ – МАРКЕР ЗА ИНО ВАЦИИ И ТЕХН ОЛОГИЧЕН Т РАНСФЕР (S UMMIT)" по ст ълб 2 „Създаване на мрежа о т изследо вателски висши училищ а" в рамките на к о мпонент „Ино ватиана България" о т Национален план за възс танов яване и ус тойчивост к ъм прог рам ата за ускоря ване на икон о мическ о то в ъзс танов яване и т рансфо рмация чрез н аука и ино вации

Energy transition – the big challenge of nowadays

New materials for the current/future needs of chemical process industries

- Oil-to-chemicals
- Methane-to-chemicals
- Methane as a transition fuel
- Renewable feedstocks
- Plastics processing
- Greenhouse gasses separation/processing
- New energy vectors

What do we need?

- Hydrothermally stable
- Ultra hydrophobic
- Ultra thermally stable
- Ultra-large pore zeolites
- Single acid site catalysis
- Improved accessibility

Going beyond the conventional zeolite comfort zone

Extending the potential applications of zeolites – thinking about tomorrow

1. Medical applications

2. Drinkable water production from air humidity

3. New materials for energy storage

4. Wastes processing

How to get what we need?

Two complementary approaches to design zeolites

Zeolite Crystal Engineering
Design "fit-for-purpose" materials from existing structures (particle size & shape, composition, added meso--& macro-porosity, defects control, Al siting…).

FAU, MOR, CHA, FER, LTL
MFI, BEA*, LTA

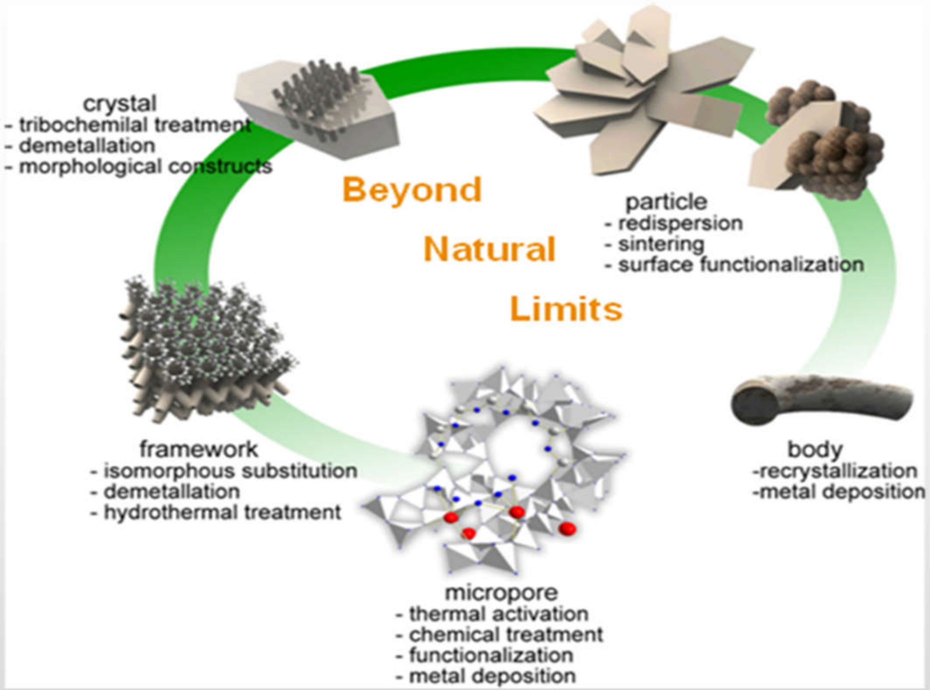
ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS	AFT	AFV	AFX
AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS	ATT	ATV	AVL	AWO	AWW
BCT	BEC	BIK	BOF	BOG	BOZ	BPH	BRE	BSV	CAN	CAS	CDO	CFI	CGF	CGS
CHA	-CHI	-CLO	CON	CSV	CZP	DAC	DDR	DFO	DFT	DOH	DON	EAB	EDI	EEI
EMT	EON	EPI	ERI	ESV	ETL	ETR	EUO	EZT	FAR	FAU	FER	FRA	GIS	GIU
GME	GON	GOO	HEU	IFO	IFR	-IFU	IFW	IFY	IHW	IMF	IRN	IRR	-IRY	ISV
ITE	ITG	ITH	ITR	ITT	-ITV	ITW	IWR	IWS	IWV	IWW	JBW	JNT	JOZ	JRY
JSN	JSR	JST	JSW	KFI	LAU	LEV	LIO	-LIT	LOS	LOV	LTA	LTF	LTJ	LTL
LTN	MAR	MAZ	MEI	MEL	MEP	MER	MFI	MFS	MON	MOR	MOZ	MSE	MSO	MTF
MTN	MTT	MTW	MVY	MWF	MWW	NAB	NAT	NES	NON	NPO	NPT	NSI	OBW	OFF
OKO	OSI	OSO	OWE	-PAR	PAU	PCR	PHI	PON	POS	PSI	PUN	RHO	-RON	RRO
RSN	RTE	RTH	RUT	RWR	RWY	SAF	SAO	SAS	SAT	SAV	SBE	SBN	SBS	SBT
SEW	SFE	SFF	SFG	SFH	SFN	SFO	SFS	SFW	SGT	SIV	SOD	SOF	SOS	SSF
SSY	STF	STI	STT	STW	-SVR	SVV	SZR	TER	THO	TOL	TON	TSC	TUN	UEI
UFI	UOS	UOV	UOZ	USI	UTL	UWY	VET	VFI	VNI	VSV	WEI	-WEN	YUG	ZON

Find a New Framework Type
You may hit the jackpot and discover a new material with unique properties.

MWW, TON, MTT,
MFI, BEA*, LTA

Our approach: Zeolite Crystal Engineering

- Customized zeolite synthesis
  - Control of zeolite crystal size and morphology
- Post-synthesis modification of zeolites properties
  - Modification of zeolite framework composition
  - Generation of mesopore to improve the intercrystalline diffusion
- Combining customized zeolite synthesis with post-synthesis modification to obtain the desired material
- Development of new synthetic methods

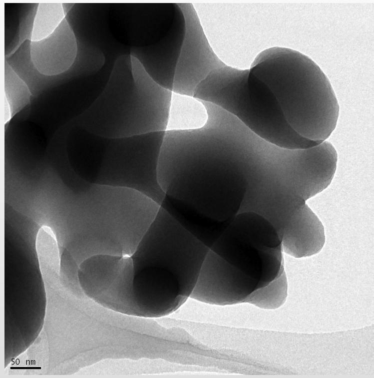


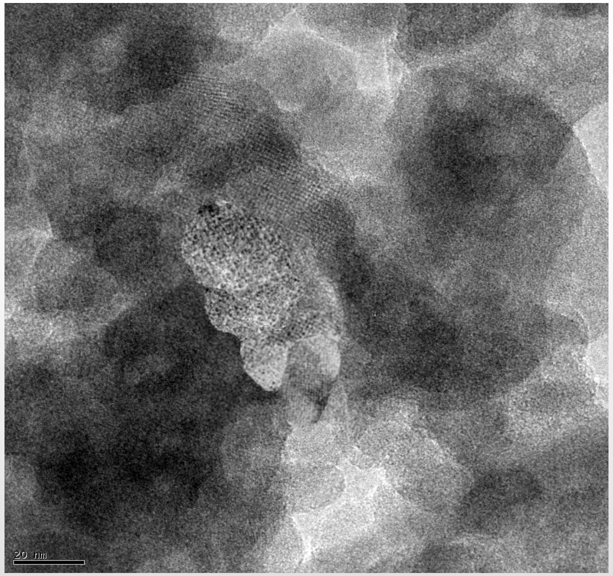
In-situ control of zeolite crystal size

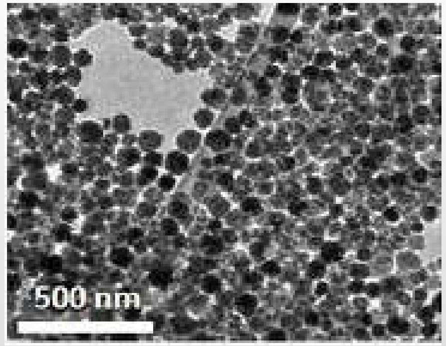
- **Which stage of gel evolution are the viable nuclei formed at?**
- **What is the spatial and temporal location of the nucleation events?**

The zeolite crystal size determines:

- The diffusion pathway
  The accessibility to the active sites
  The adsorption/desorption kinetics
- The external surface area







Science, 1999, *238*, 958; **J. Phys. Chem. B** 2004, *108*, 15587; **J. Am. Chem. Soc.** 2005, *127*, 16171; **Langmuir** 2005, *21*, 10724; **Micropor. Mesopor. Mater.** 2007, *101*, 73; **J. Am. Chem. Soc.** 2009,*131*, 10127; **Chem .– A Eur. J.** 2011, *17*, 2199; **Chem .– A Eur. J.** 2015, *21,* 18316; **J. Am. Chem. Soc.** 2021, *143, 1993.*

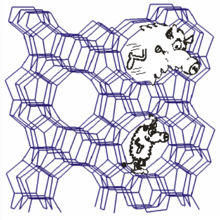
Финансирано от Европейския съюз
NextGenerationEU

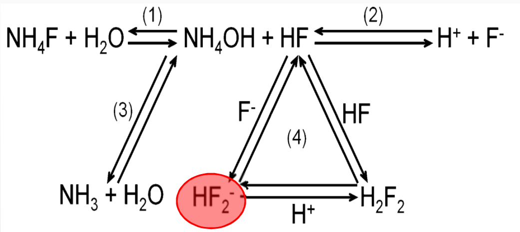
SUMMIT
SOFIA UNIVERSITY MARKING MOMENTUM FOR INNOVATION AND TECHNOLOGICAL TRANSFER

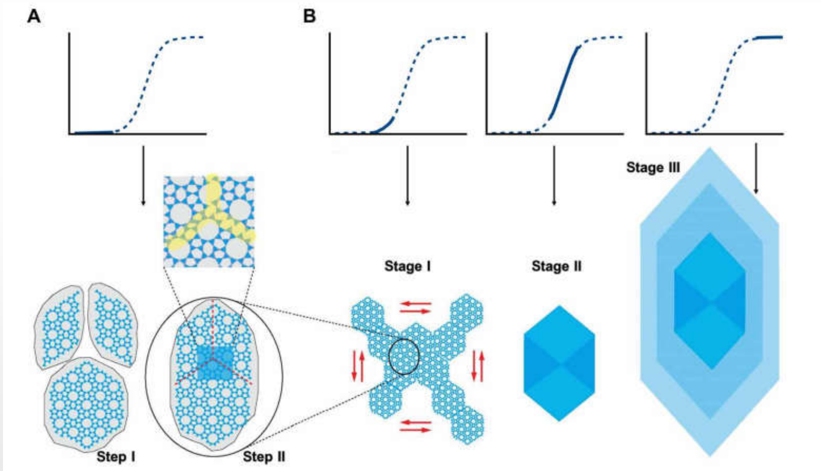
СОФИЙСКИ УНИВЕРСИТЕТ - МАРКЕР ЗА ИНОВАЦИИ И ТЕХНОЛОГИЧЕН ТРАНСФЕР

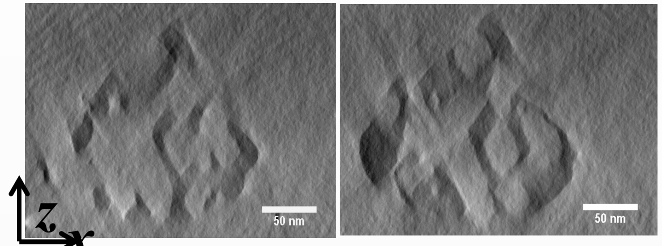
Национален план за възстановяване и устойчивост
НА РЕПУБЛИКА БЪЛГАРИЯ

Post-synthesis control of active sites accessibility in zeolites

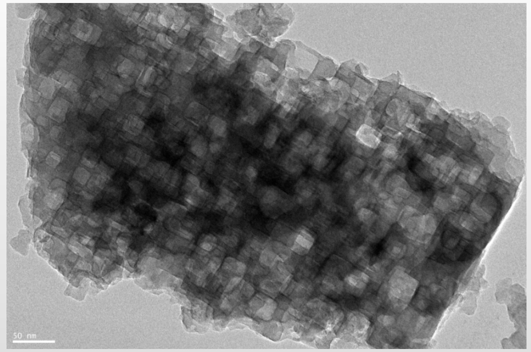








TEM tomography slices of FHF$^-$ etched ZSM-5



Open the route to:

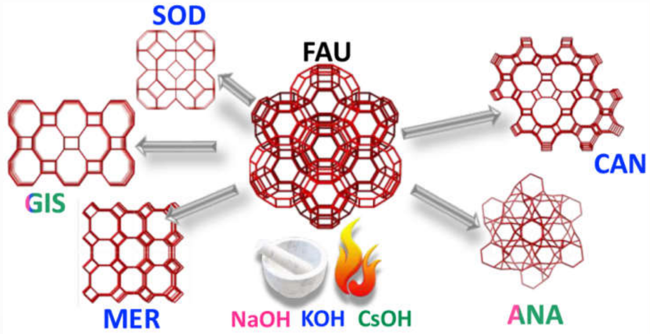
- Decrease the impact of the diffusion limitations
- Healing the defect sites
- Incorporation of catalytically active species
- Retaining only the coherent domains in a zeolite crystal

Advanced Science 2022, 9, 2104414; **Advanced Science** 2021, 2100001; **Science Advances** 2021, 7, eabg0454; **J. Am. Chem. Soc.** 2017, 139 (48), 17273-17276; **Angew. Chem.** 2016, 55, 15049-15052; **Chem. Mater.** 2013, 25, 2759-2766.

First results

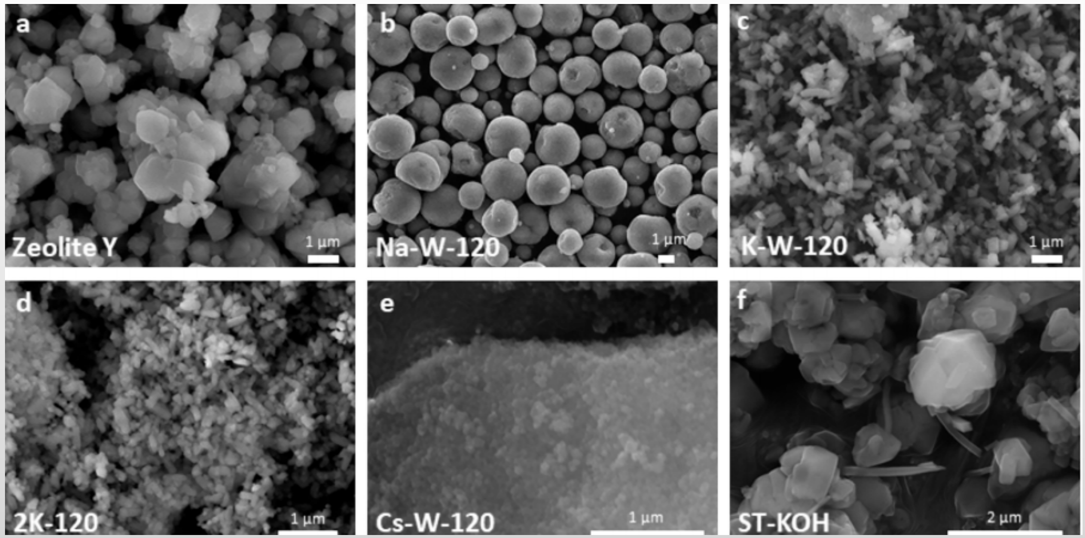
Title: Mechanochemically Induced OSDA-Free Interzeolite Conversion

ACS Sustainable Chemical Engineering, 2024, accepted
DOI: https://doi.org/10.1021/acssuschemeng.3c08477



Summary

- Mechanochemical processing under controlled elevated temperatures allowed for rapid, efficient, and controllable solid-state interzeolite conversion without added OSDAs.
- Milling FAU-type zeolite Y with alkali hydroxides at 110 °C afforded three phase-pure crystalline products (ANA, MER, and CAN), mixtures of several zeolite phases, and an amorphous phase that was detected in some products.
- Our future work will focus on developing strategies to achieve the direct formation of advanced zeolite materials by mechanochemical processing and further our efforts presented herein to achieve selective interzeolite conversions.



До говор BG-RRP-2.004-0008 за финанси ране на проект „СОФИЙСКИ УНИВЕРСИТЕТ – МАРКЕР ЗА ИНО ВАЦИИ И ТЕХН ОЛОГИЧЕН Т РАНСФЕР (S UMMIT)“ по ст ълб 2 „Създаване на мрежа о т изследо вателски висши училищ а“
в рамките на к о мпонент „Ино вативна България“ о т Национален план за възс танови ване и ус тойчивост к ъм прог рам ата за ускоря ване на икон о мическ о то в ъзс танови ване и т рансфо рмация чрез н аука и ино вации

SUMMIT

SOFIA UNIVERSITY
MARKING MOMENTUM
FOR INNOVATION AND
TECHNOLOGICAL TRANSFER

Финансирано от
Европейския съюз
NextGenerationEU

Национален план за
възстановяване и устойчивост
НА РЕПУБЛИКА БЪЛГАРИЯ

Thank you for your attention