Effect of zeolite type on activity of MoS_2/Al_2O_3-Z catalysts in hydroconversion of methylpalmitate

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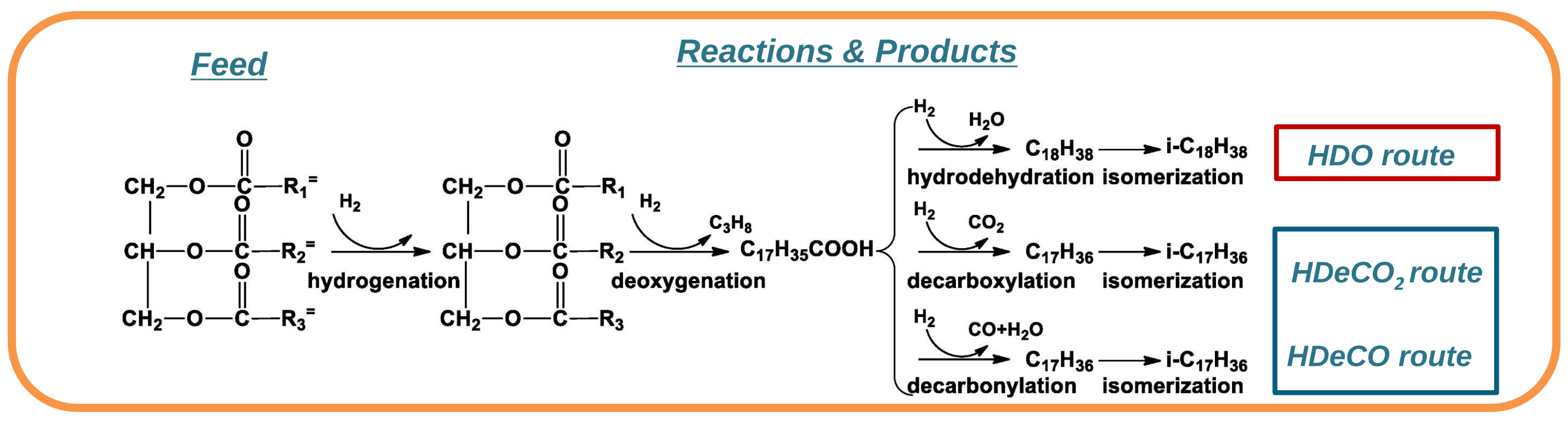
Introduction

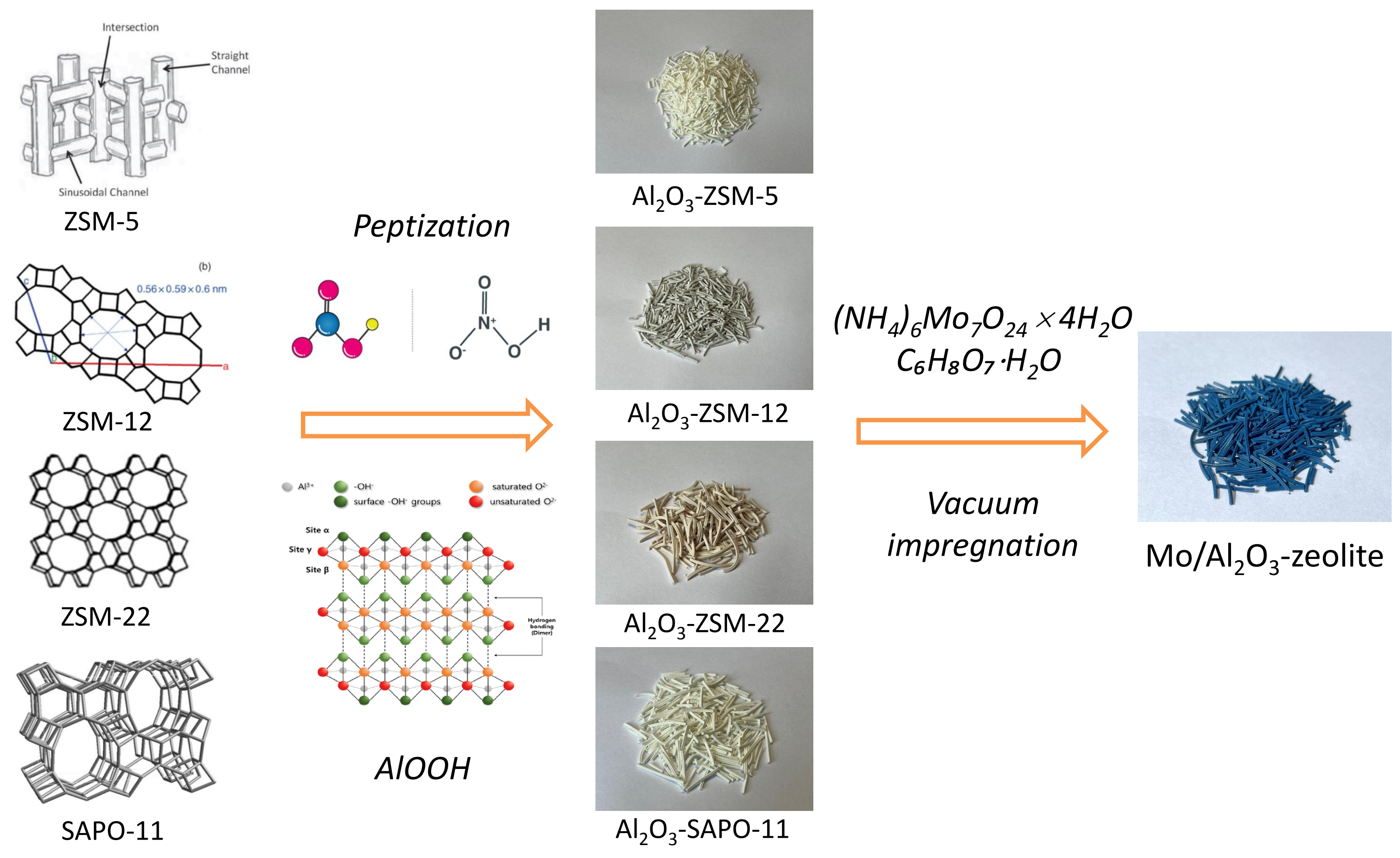


The deterioration of climatic conditions associated with increased greenhouse gas emissions and the depletion of fossil resources stimulate the search for alternative energy sources. In recent years, the isomerization and hydrogenation of fatty acid esters has attracted great interest from researchers. One of the main applications of this reaction is the production of fuel from biomass.

Vegetable oils (non-edible oils, waste oils, etc.) containing triglycerides of fatty acids can serve as a source of components of bio-jet (C_8-C_{15} alkanes). Typically, the process for obtaining bio-jet kerosene components consists of two stages: hydrodeoxygenation (sulfide catalysts) and isomerization/cracking (noble metals on acid carriers). The use of ***a one-stage process*** for the hydroprocessing of fatty acid triglycerides into components of bio-jet fuel will reduce capital and operating costs, avoid an intermediate purification stage, simplify process control, and reduce energy and hydrogen consumption.

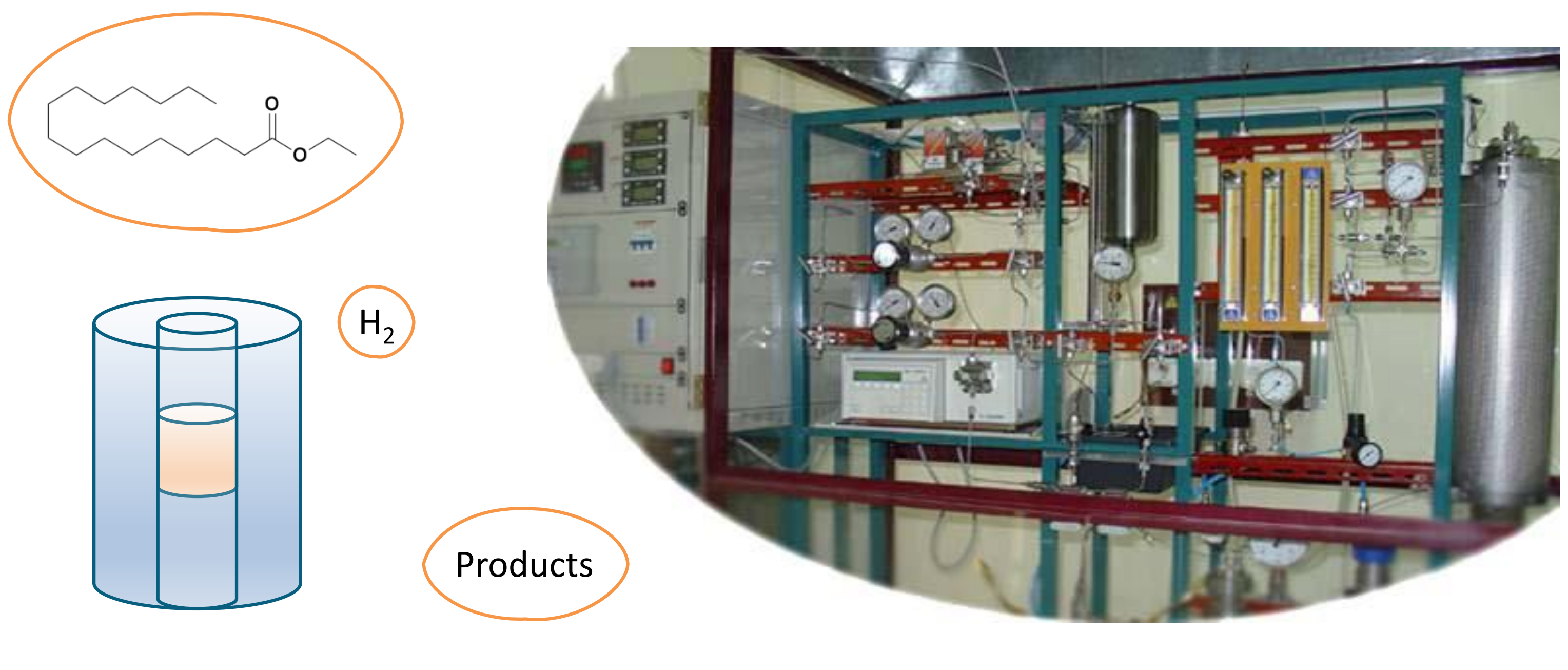
Therefore, the development of polyfunctional catalysts that ensure the occurrence of several reactions simultaneously (HDO, hydroisomerization, and hydrocracking) to obtain a product of a given composition is a promising line of research that has been actively developed in recent years.

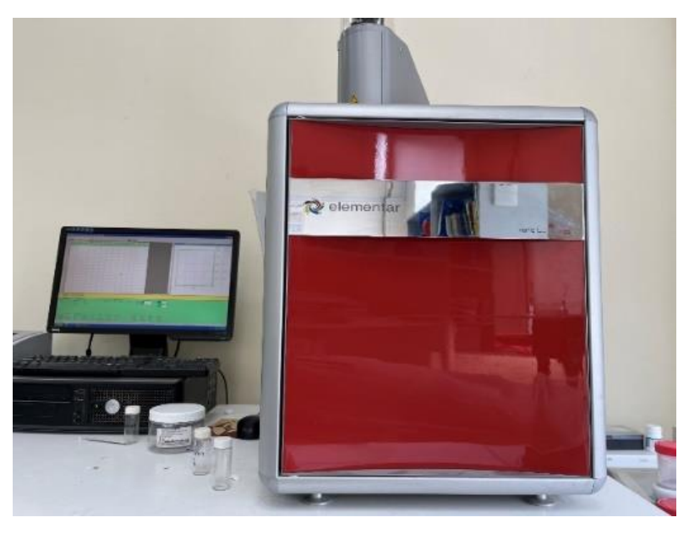
Preparation of the supports and catalysts



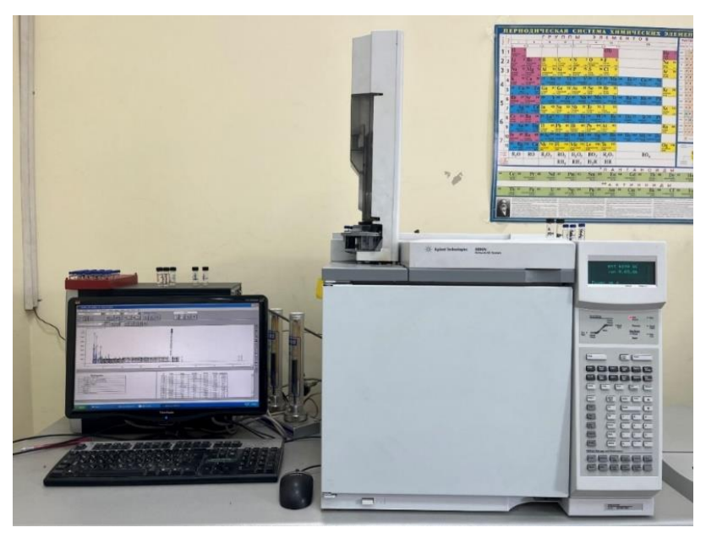
Catalyst	Mo, масс.%	Support	Texture characteristics of the supports		
			S_{area}, m^2/g	V_{pore}, cm^3/g	D_{pore}, nm
Mo/Al_2O_3	6,95	Al_2O_3	142	0,66	25,1
Mo/Al-Z5	6,90	Al_2O_3-ZSM-5	202	0,48	25,6
Mo/Al-Z12	6,96	Al_2O_3-ZSM-12	165	0,49	22,8
Mo/Al-Z22	6,90	Al_2O_3-ZSM-22	175	0,53	25,5
Mo/Al-SAPO-11	6,97	Al_2O_3-SAPO-11	177	0,42	22,6

Experimental





Total oxygen content



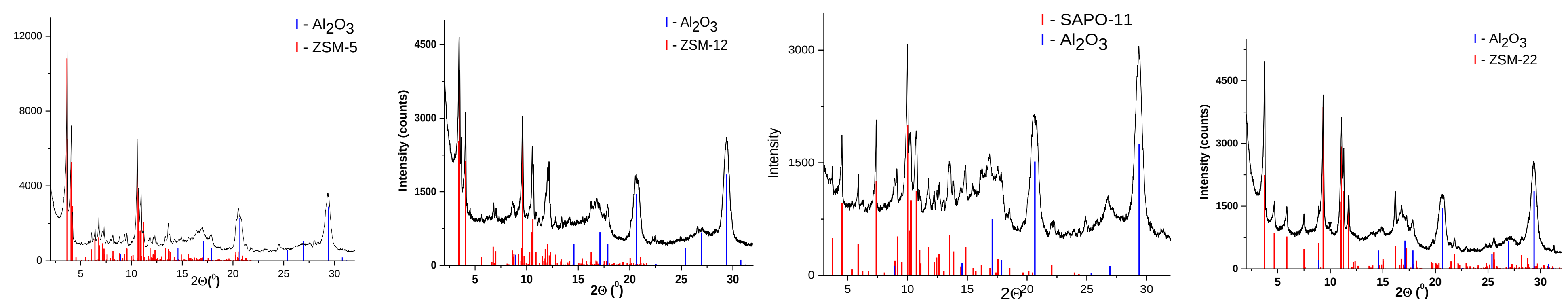
Analysis of liquid MP conversion products

Analysis of the gas phase

	Temperature/℃	Pressure/ MPa	LHSV/ h^{-1}	H_2/feedstock
Sulfidation	340	3.5		
Hydrodeoxygenation	250-350	3.0	36	600
Hydroisomerization	at least 310	3.0-5.0	36	600
Feedstock	10 wt.% of methylpalmitate in dodecane (1.17 wt.% O)			
Catalyst loading volume	0.25-0.5 mm size fraction (0.5ml)			

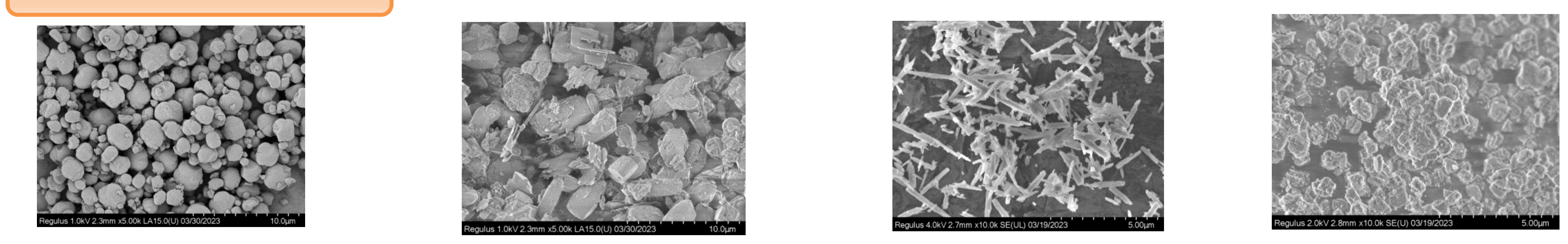
Characterization of the supports and catalysts

XRD



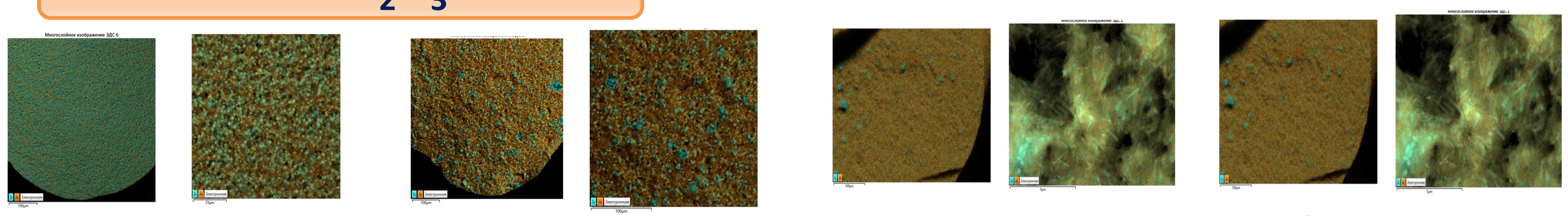
- *Zeolite phases ZSM-5,ZSM-12,ZSM-22 and silicoaluminophosphate SAPO-11 are retained in the supports*

SEM of zeolites



ZSM-5 ZSM-12 ZSM-22 SAPO-11

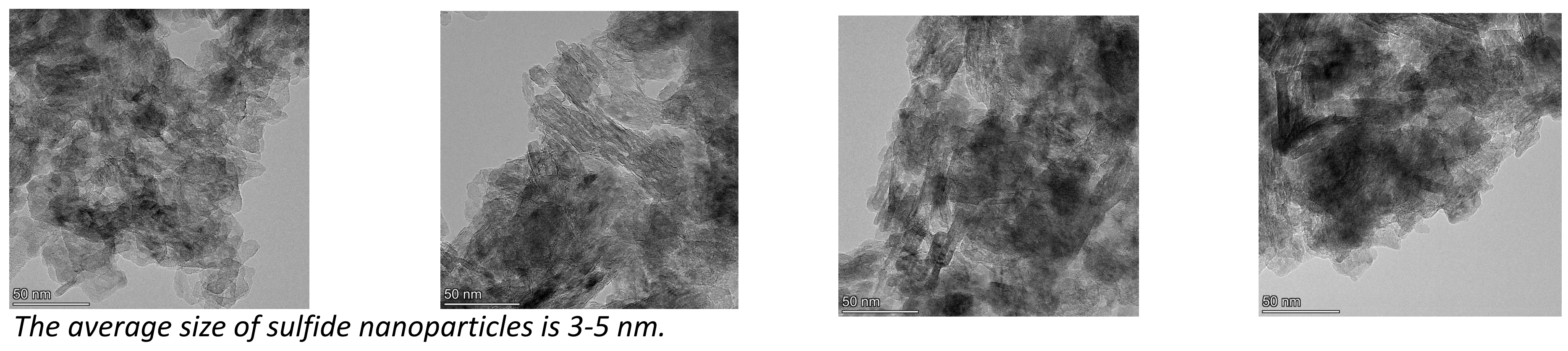
SEM-EDX of Al_2O_3-zeolite



Al_2O_3-ZSM-5 Al_2O_3-ZSM-12 Al_2O_3-ZSM-22 Al_2O_3-SAPO-11

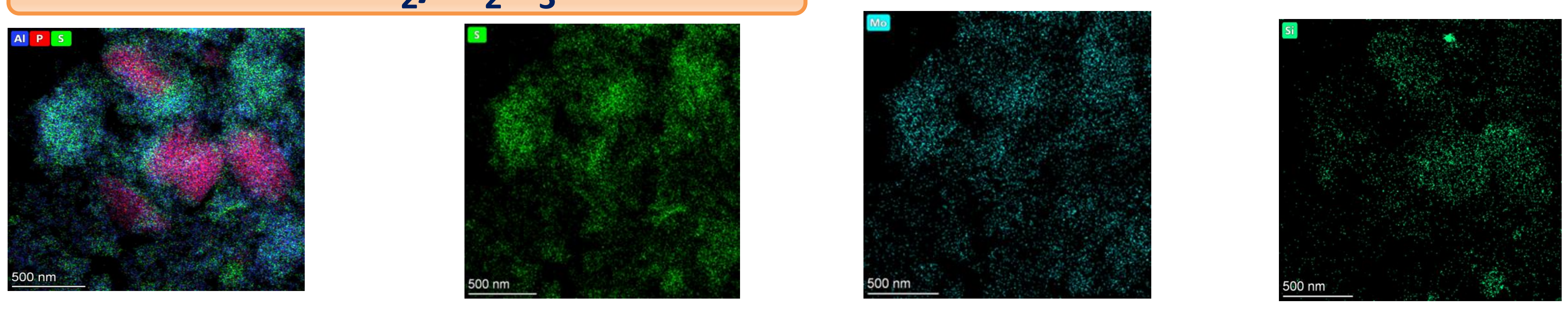
- ***Zeolite particles are evenly distributed on the support.***

TEM of MoS_2/Al_2O_3-zeolite



- *The average size of sulfide nanoparticles is 3-5 nm.*

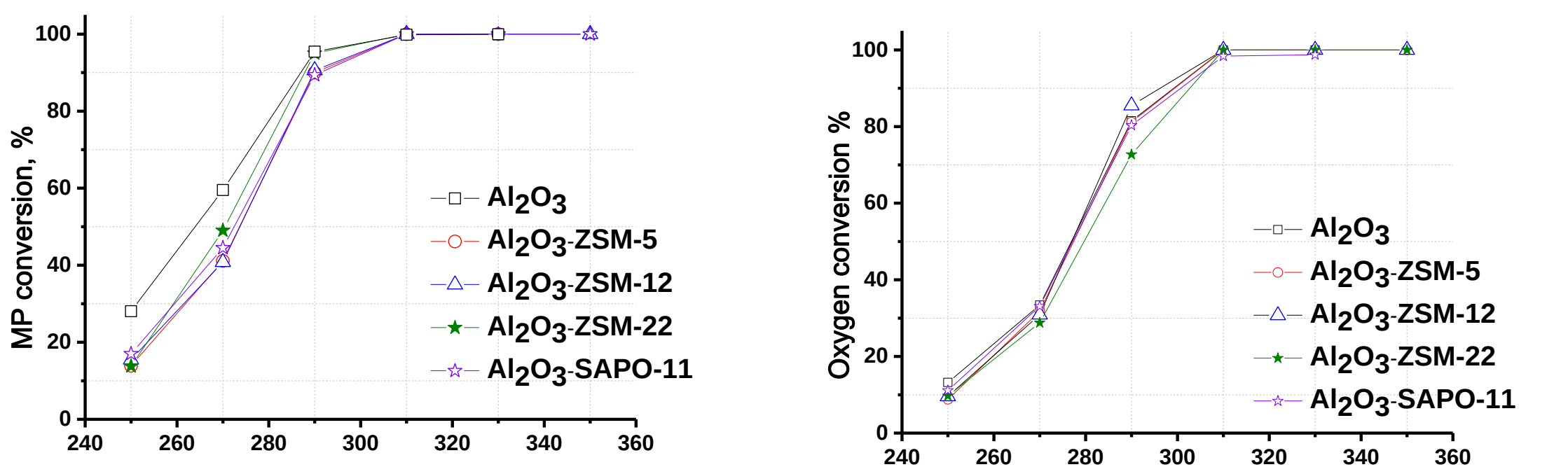
TEM-EDX of MoS_2/Al_2O_3-SAPO-11



- *The MoS_2 particles are predominantly distributed on the surface of the alumina.*

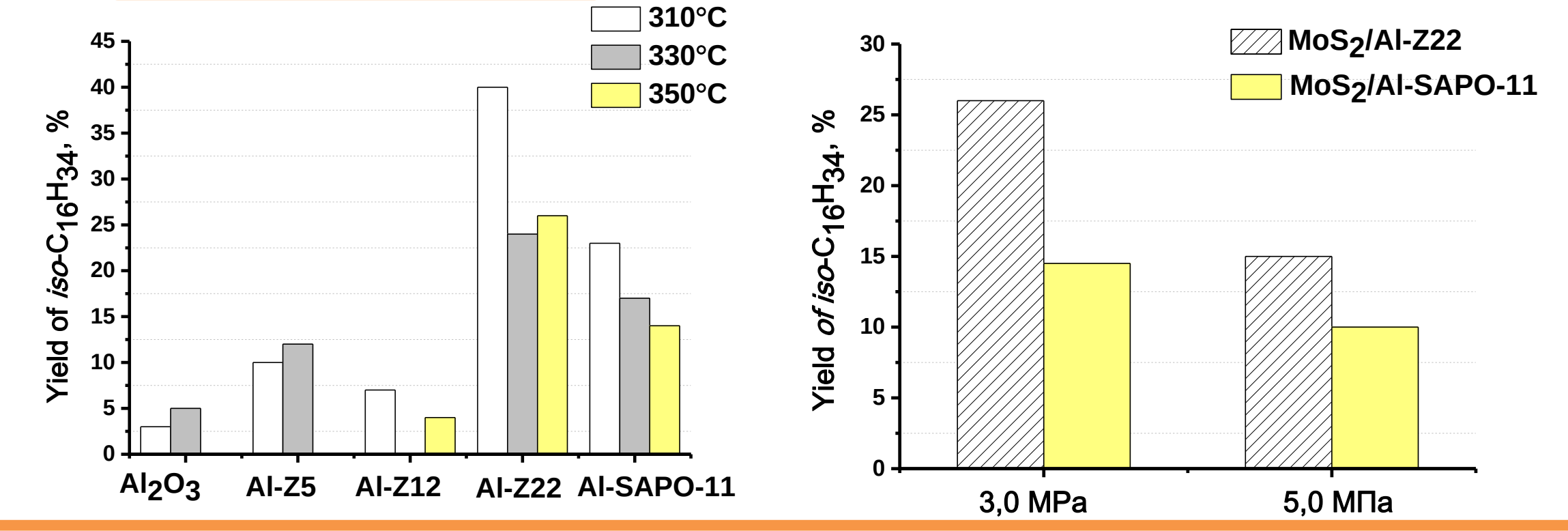
Catalytic activity

Hydrodeoxygenation



- **Complete conversion of O-containing is observed at 310℃ and higher.**

Hydroisomerization



- **Yield of iso-$C_{16}H_{34}$: Al_2O_3<Al-Z12<Al-Z5<Al-SAPO-11<Al-Z22**
- **Reduction of sulfide catalyst activity with increasing pressure and temperature.**

Conclusions

A comparative study of sulfide Mo catalysts showed that the introduction of zeolites leads to an increase in MP conversion by 10–15% in all temperature range (due to a rate increase of the acid-catalyzed ester hydrolysis reaction) and a decrease in the selectivity of the formation of C_{16} alkanes due to decarbonylation reaction. 100% conversion of oxygen-containing compounds is achieved at a temperature of 310° C. The highest yield of *iso*-alkanes was observed for ZSM-22 containing catalyst.

Acknowledgements

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