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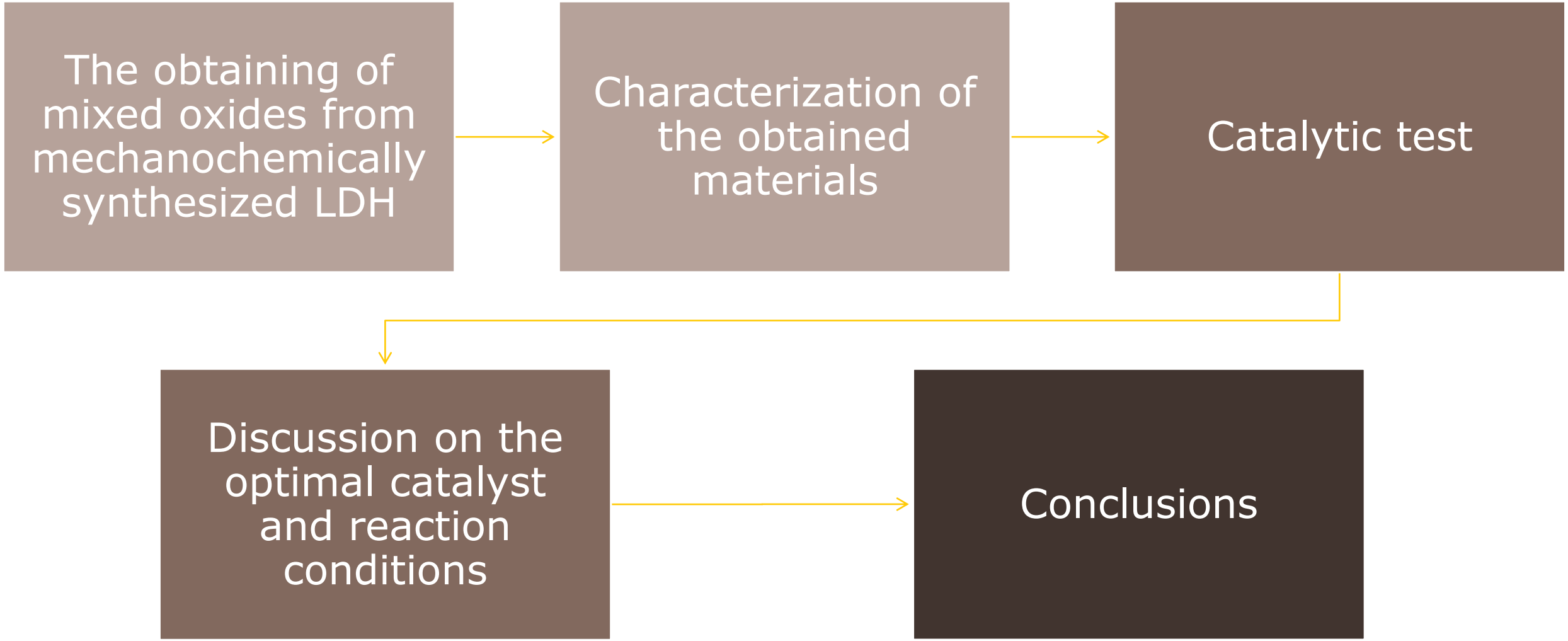
A Comparative Study on the Catalytic Activity of Mixed Oxides Derived from LDH in the Synthesis of Methylpyrazine

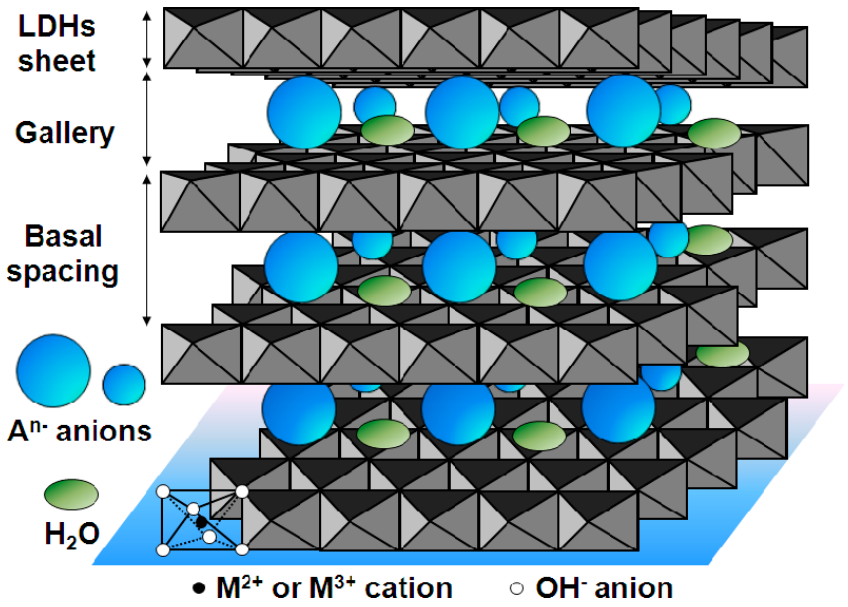
Florina Teodorescu[1], Andrei Slabu[1], Octavian D. Pavel[2]

[1]„C.D. Nenitzescu" Center for Organic Chemistry, Romanian Academy
[2]University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis


The obtaining of mixed oxides from mechanochemically synthesized LDH
Characterization of the obtained materials
Catalytic test
Discussion on the optimal catalyst and reaction conditions
Conclusions

Layered Double Hydroxides (LDH)

- LDH - $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}]\cdot mH_2O$



- M^{2+} and M^{3+} - divalent and trivalent cations in the brucite-type layers
- *A* is the interlayer anion with a n charge balancing the exceeding charge occurring by isomorphic substitution of M^{2+} by M^{3+}
- *x* is the fraction of the trivalent cation
- *m* is the crystallization water

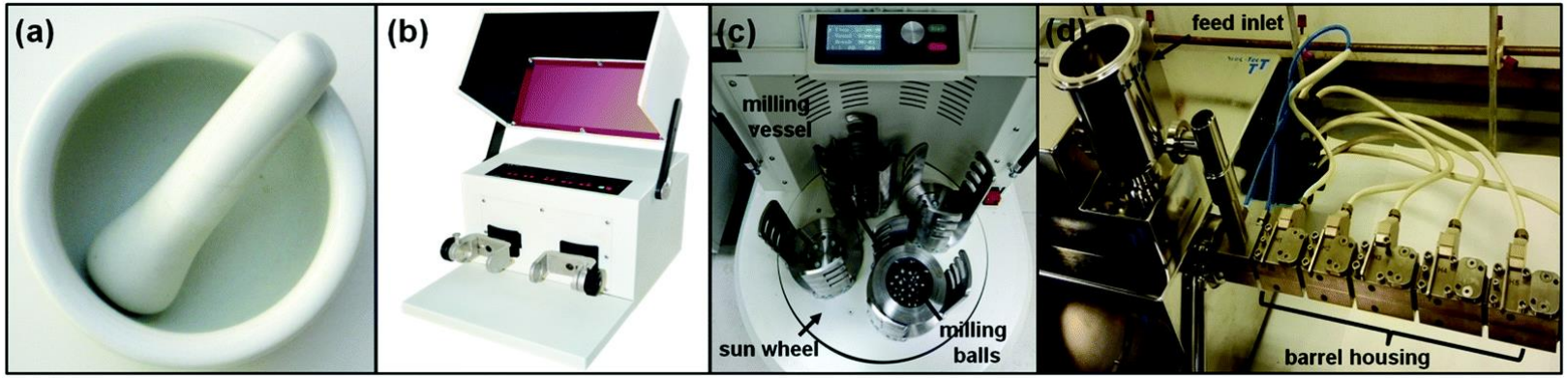
X. Bi, H. Zhang, L. Dou, *Pharmaceutics* **2014**, *6*(2), 298-332

Mechanochemistry

Mechanochemistry - first introduced by Ostwald in 1891 and defines a mechanochemical reaction as "**a chemical reaction induced by mechanical energy**"

Applications:

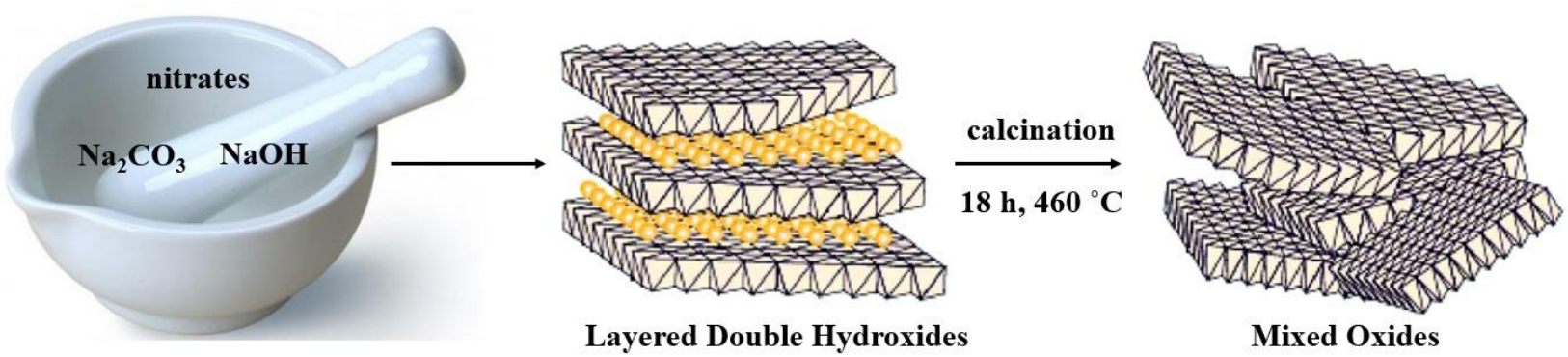
- Organic Chemistry
- Supramolecular Chemistry
- Organometallics
- Polymers
- **Inorganic Chemistry**
- Nanoparticles



(a) mortar and pestle, (b) electric shaker mill, (c) planetary mill and (d) twin-screw extruder.

D. Tan, F. Garcia, *Chem. Soc. Rev.* **2019**, 48, 2274-2292

From LDHs to mixed oxides



Mixed oxides

- High surface area
- Higher number of catalytic sites
- Thermal stability
- Possibility of regeneration

- **M^{2+} = Zn, Co, Ni**
- **M^{3+} = Al**

A. I. Slabu, O. D. Pavel, F. Teodorescu, *Catal. Commun.*, under review

Characterization of the catalysts

The XRD patterns of samples (A – layered double hydroxides;
B – mixed oxides obtained by calcination of LDH)

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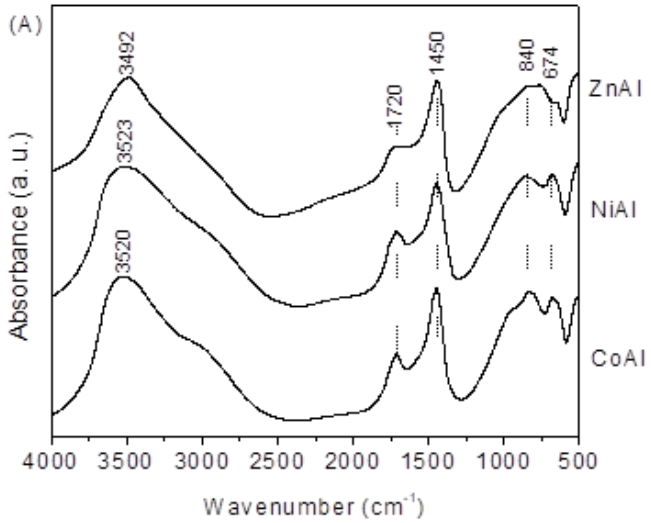
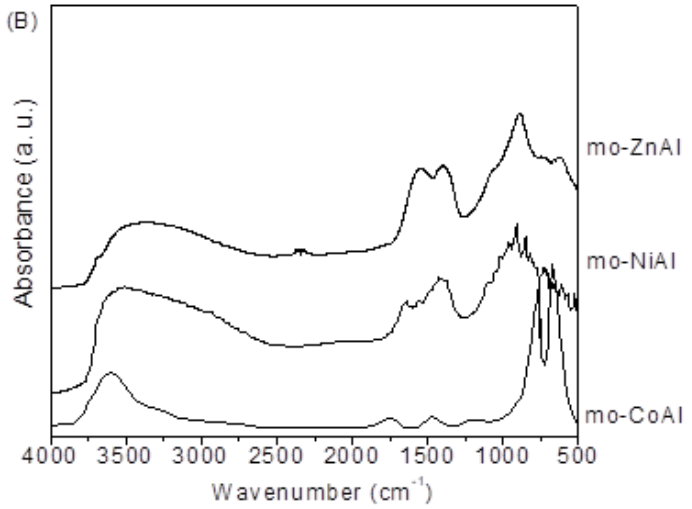
Characterization of the catalysts





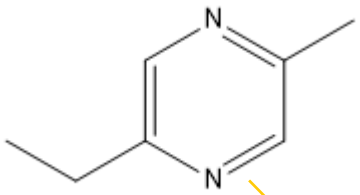
DRIFT spectra of samples (A – layered double hydroxides;
B – mixed oxides obtained by calcination of LDH)

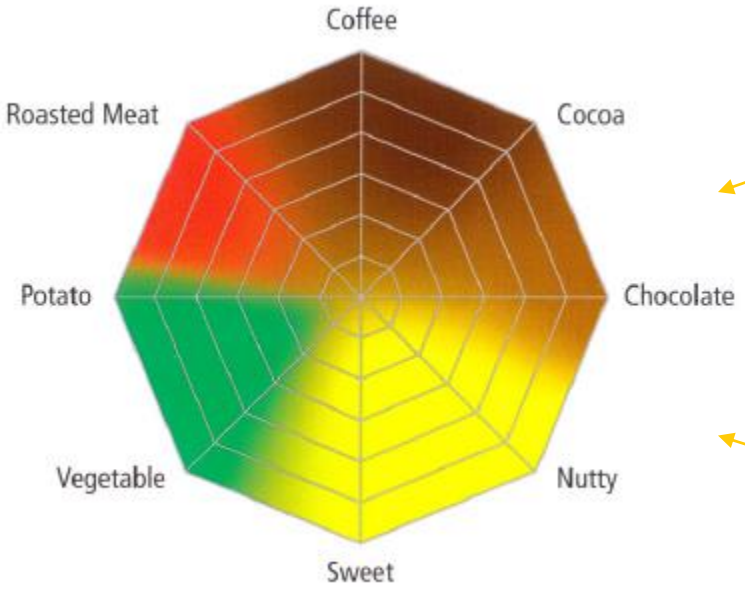
Materials		Specific surface (m^2/g)	Acidity (mmol NH_3/g)	Basicity (mmol CO_2/g)
LDH	Ni/Al	87	-	-
	Zn/Al	91	-	-
	Co/Al	102	-	-
Mixed oxides	Ni/Al	131	2.1	1.4
	Zn/Al	128	1.1	1.3
	Co/Al	151	2.9	1.6

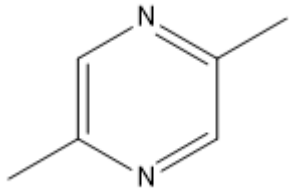
The textural properties of the LDH and of the mixed oxides obtained by calcination of LDH

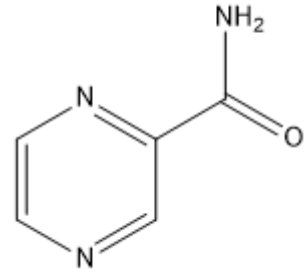
A. I. Slabu, O. D. Pavel, F. Teodorescu, *Catal. Commun.*, under review

Alkylpyrazines and their uses

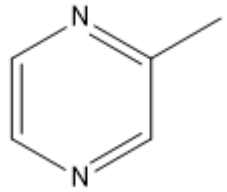








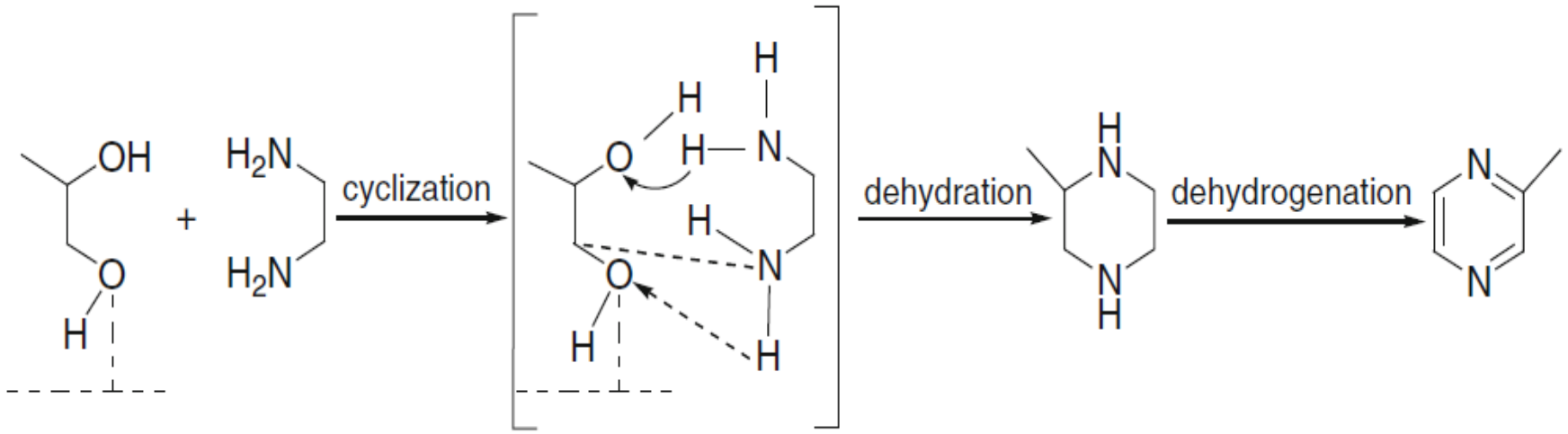
Pyrazinamide
(antitubercular drug)



Methylpyrazine

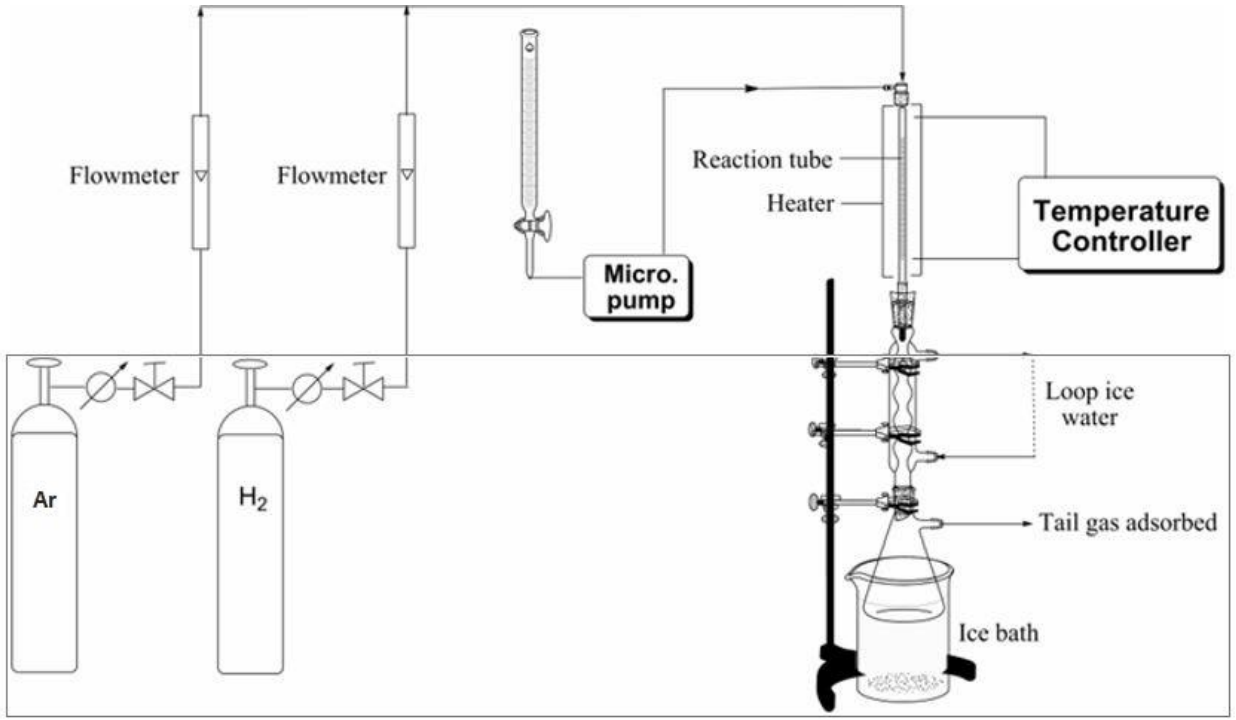
The cyclodehydrogenation reaction

The Eley-Rideal mechanism on a bifunctional solid catalyst



S. Nestori, L. Forni, *Heterogenous Catalysis and Fine Chemicals*, pp. 291-298, 1988.

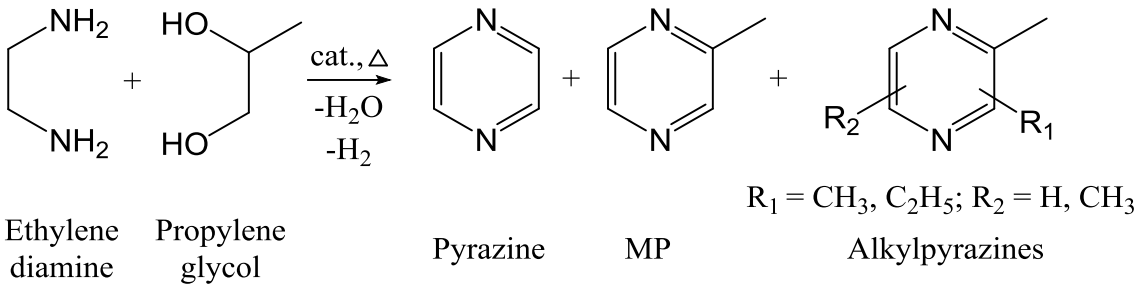
Reaction system for the synthesis of methylpyrazine



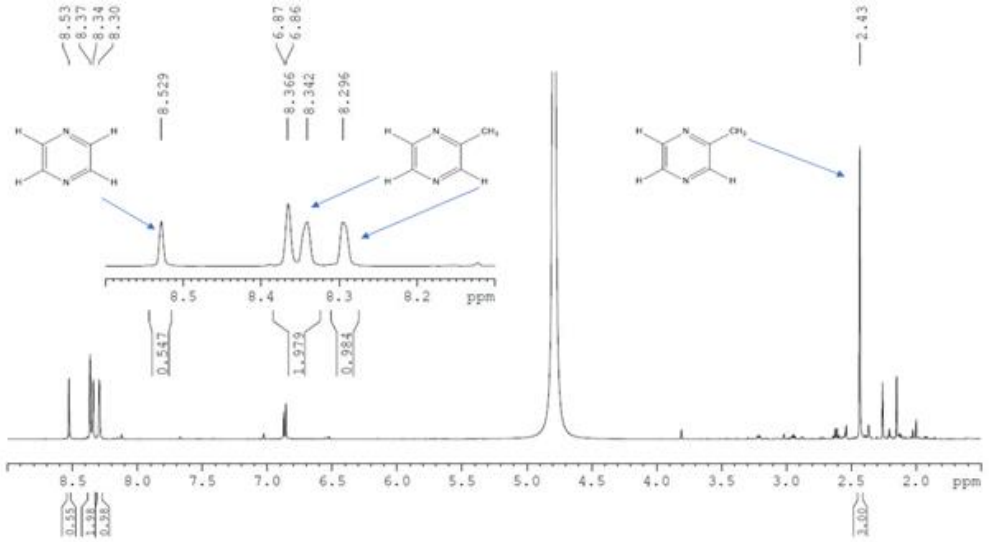
Catalyst activation: 400 °C, 2 h, gas mixture Ar:H_2 = 1:1 (vol.), gas flow rate = 20 mL/min, t = 2 h;

Reaction: 400 °C, reactant mixture 50% water (vol.), reactant flow rate = 1 mL/h, Ar carrier gas, gas flow rate = 10 mL/min

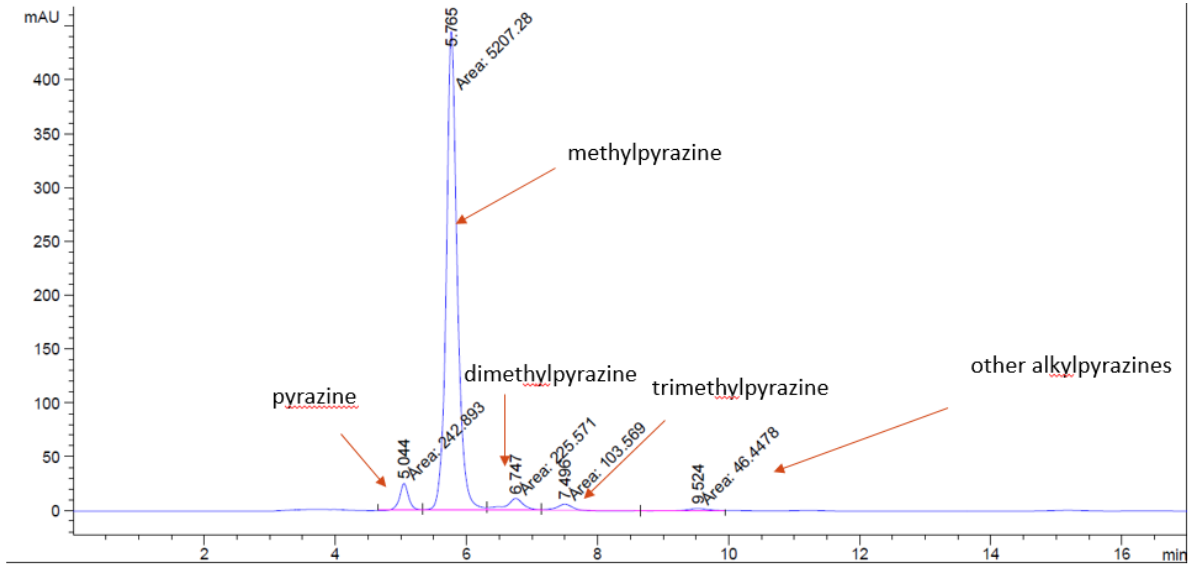
Catalytic activity testing



$R_1 = CH_3, C_2H_5; R_2 = H, CH_3$

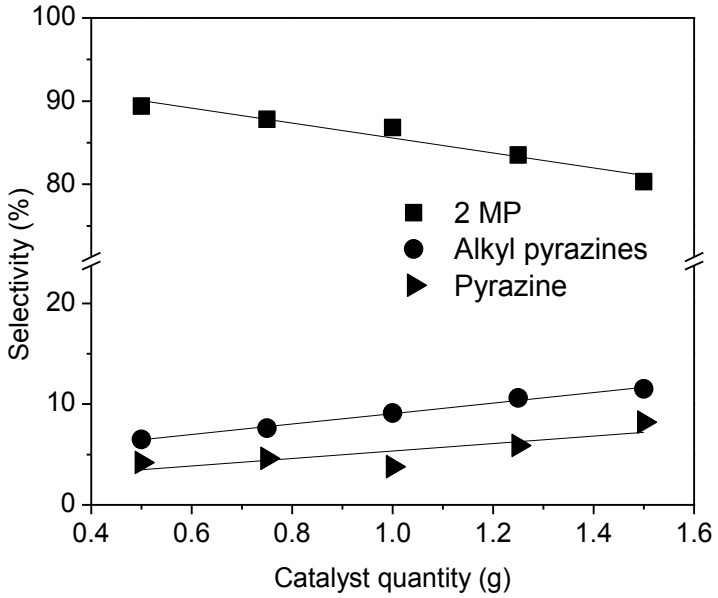


- Varian Gemini 300 BB, 300 and 75 MHz, D_2O solvent

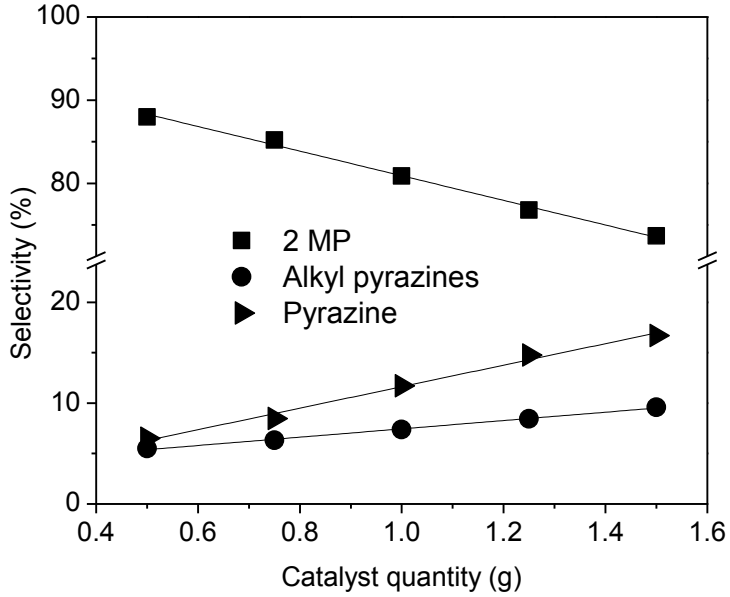


- HPLC Agilent Chromatograph 1200 Series
- Agilent Zorbax SB-C18(250x4.6) column
- H_2O/ACN = 30/70 (vol.)
- 0,6 mL/min flow rate
- column temperature = 40 °C

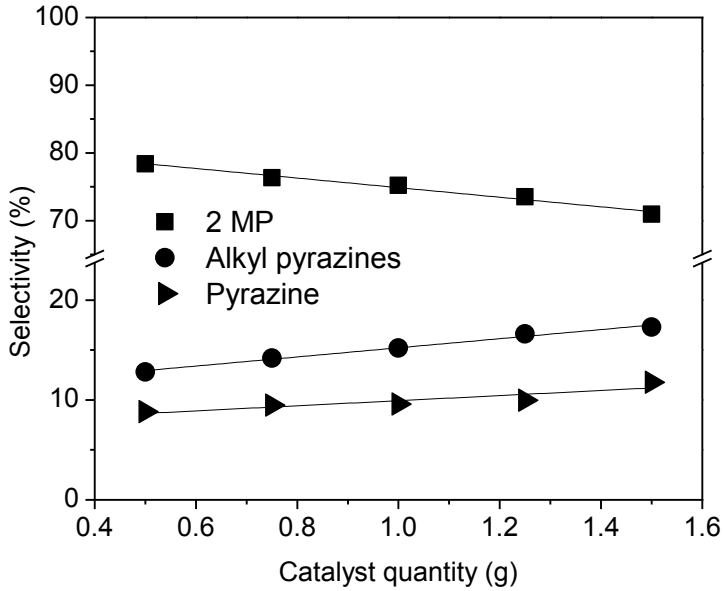
Discussion



mo-ZnAl



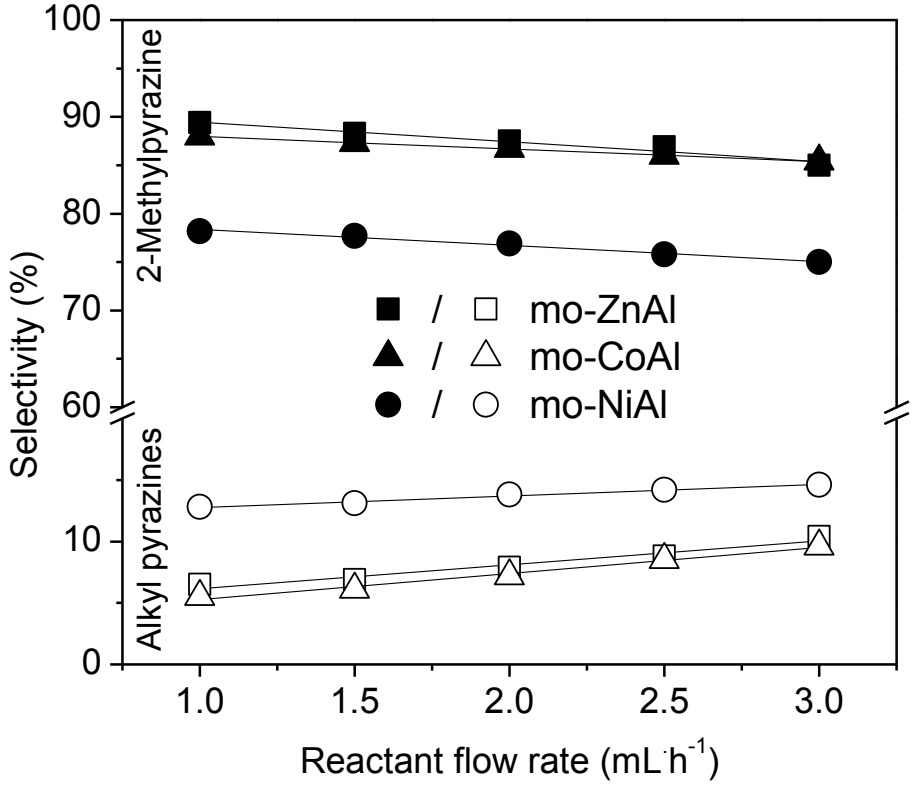
mo-CoAl



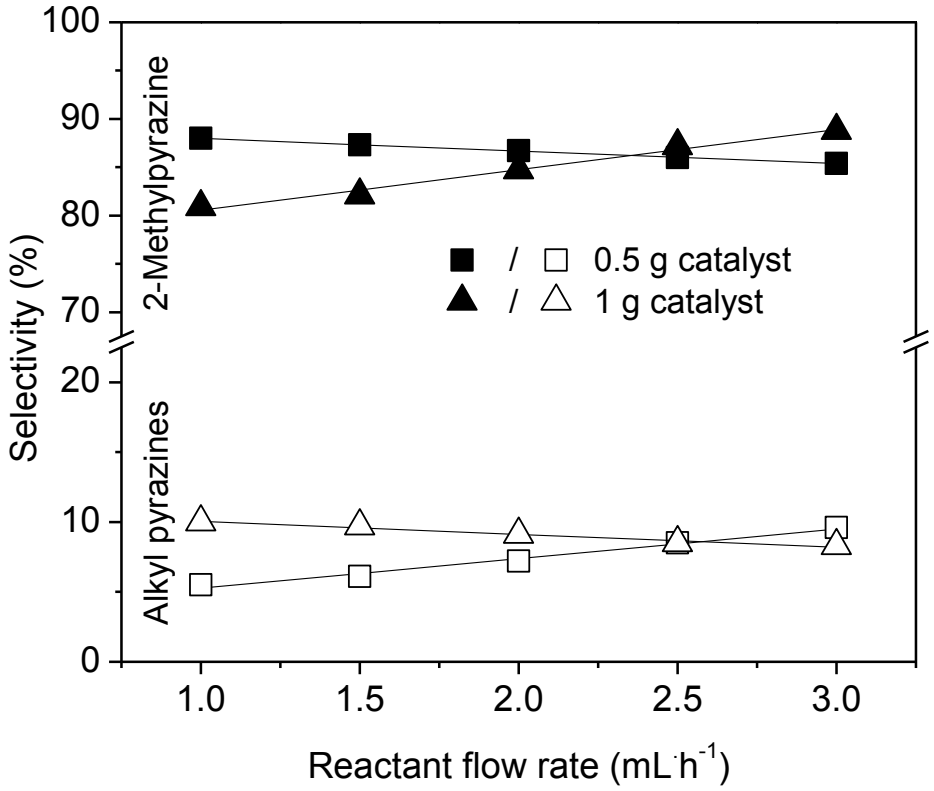
mo-NiAl

Influence of catalyst quantity for the 3 mixed oxides used on pyrazine compounds selectivity at a reaction temperature of 400 °C. Flow rate of reaction mixture 1 $mL \cdot h^{-1}$

Discussion



Influence of the reactant flow rate on pyrazine compounds selectivity, for all three materials, at a reaction temperature of 400 °C, over 0.5 g of catalyst.



Influence of the reactant flow rate on pyrazine compounds selectivity, over different CoAl catalyst loadings

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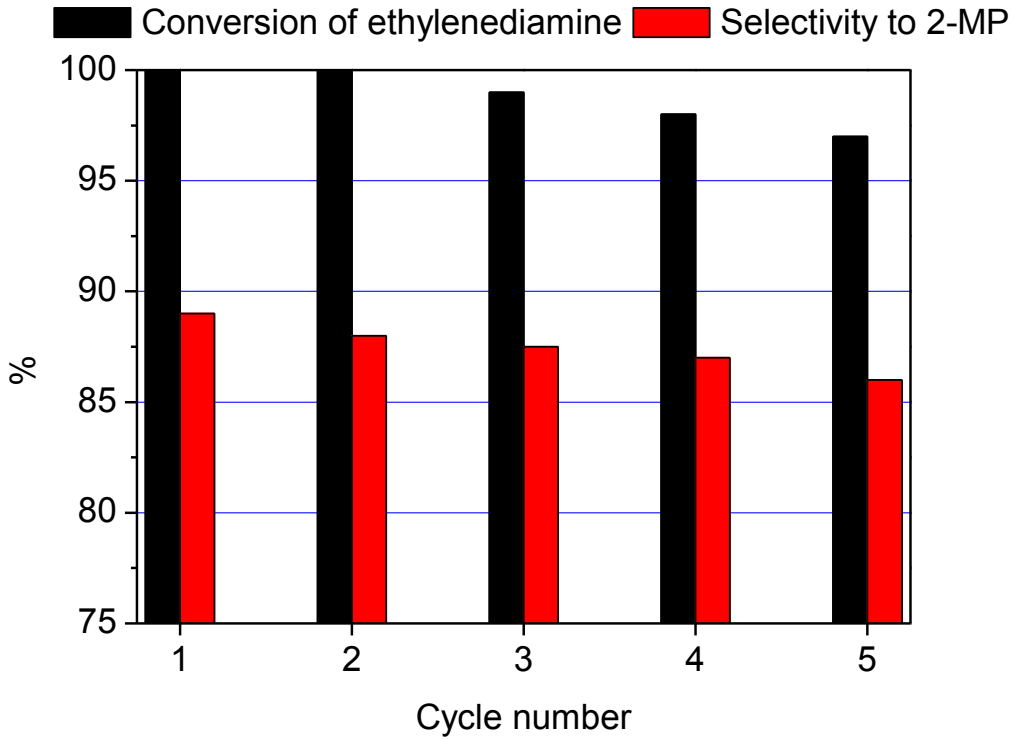
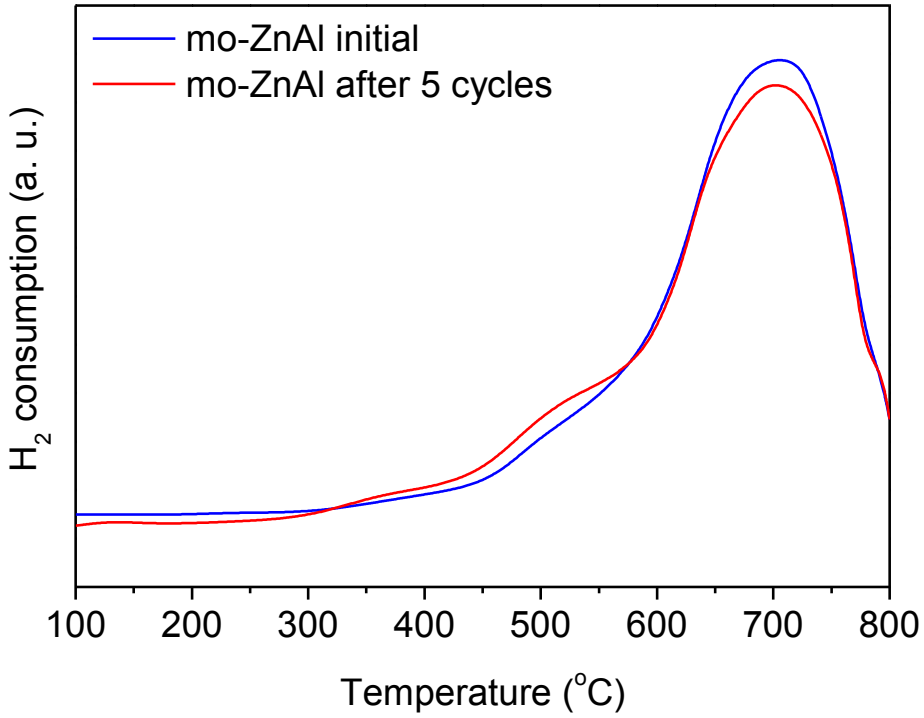
Discussion



The variation of the catalytic performances in 5 reaction cycles under the same conditions (reaction temperature of 400 °C, 0.5 g of catalyst, reactant flow rate 1 mL·h^{-1})



TPR profile for the fresh mo-ZnAl compared to the one obtained after being utilized in 5 consecutive reaction cycles

A. I. Slabu, O. D. Pavel, F. Teodorescu, *Catal. Commun.*, under review

Conclusions

Mechanochemical method – a facile and economic route to produce LDH materials

The layered structure has been demonstrated by X-ray diffraction and DRIFT

Mixed oxides obtained from LDHs are suitable catalysts in methylpyrazine synthesis

The influence of various reaction conditions on MP selectivity has been investigated

mo-ZnAl and mo-CoAl presented better results as a consequence of the increased concentration of strong Lewis-type sites that favored the dehydration-cyclization

Thank you for your attention!

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