ALKYLPYRAZINES SYNTHESIS OVER Zn/Al MIXED OXIDE OBTAINED BY MECHANOCHEMICAL METHOD

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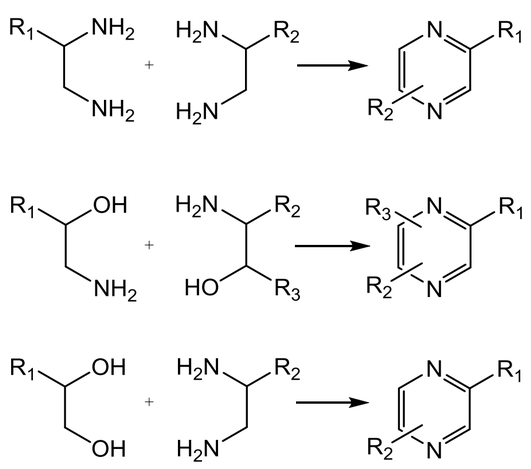
Introduction

Alkylpyrazines are a class of N-heterocyclic compounds found in the composition of natural and synthetic compounds, having a wide variety of applications (food and pharmaceutics industries). One of the most effective synthesis route is the cyclo-dehydrogenation reaction on the surface of bifunctional metal catalysts. In this study we used a Zn/Al mixed oxide (mo-Zn/Al) obtained from a layered double hydroxide (LDH) precursor, which was selected in a previous study regarding the activity of different mixed oxide catalysts in the obtaining of 2-methylpyrazine. The raw materials used on that study were a vicinal diol (propylene glycol) and a diamine (ethylene diamine). This study focused on extending towards a wider variety of alkylpyrazine compounds using different raw materials. The cyclo-dehydrogenation reactions performed were between two diamines, alkanolamines or between a diamine and a diol.

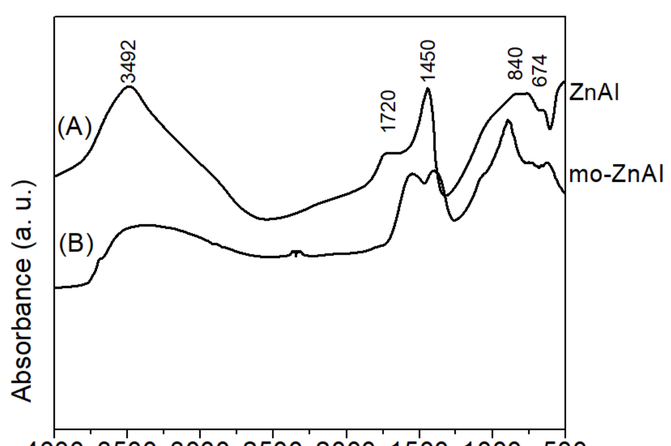
Results and discussions

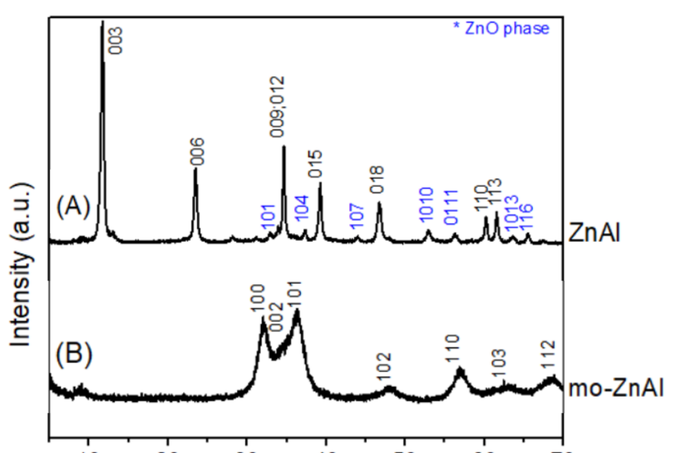
The three types of cyclo-dehydrogenation reactions performed



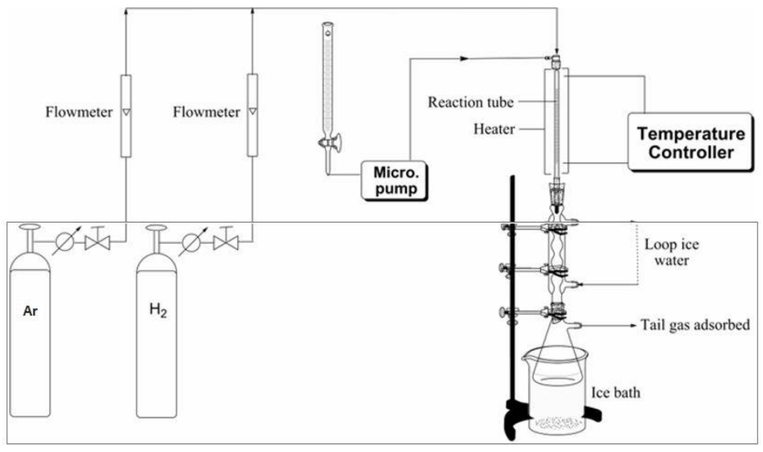
R_1 = H, -CH_3, -CH_2CH_3, R_2 = H, -CH_3, -CH_2CH_3, R_3 = H, -CH_3

DRIFT and XRD analysis for Zn/Al LDH (A) and mo-Zn/Al (B)





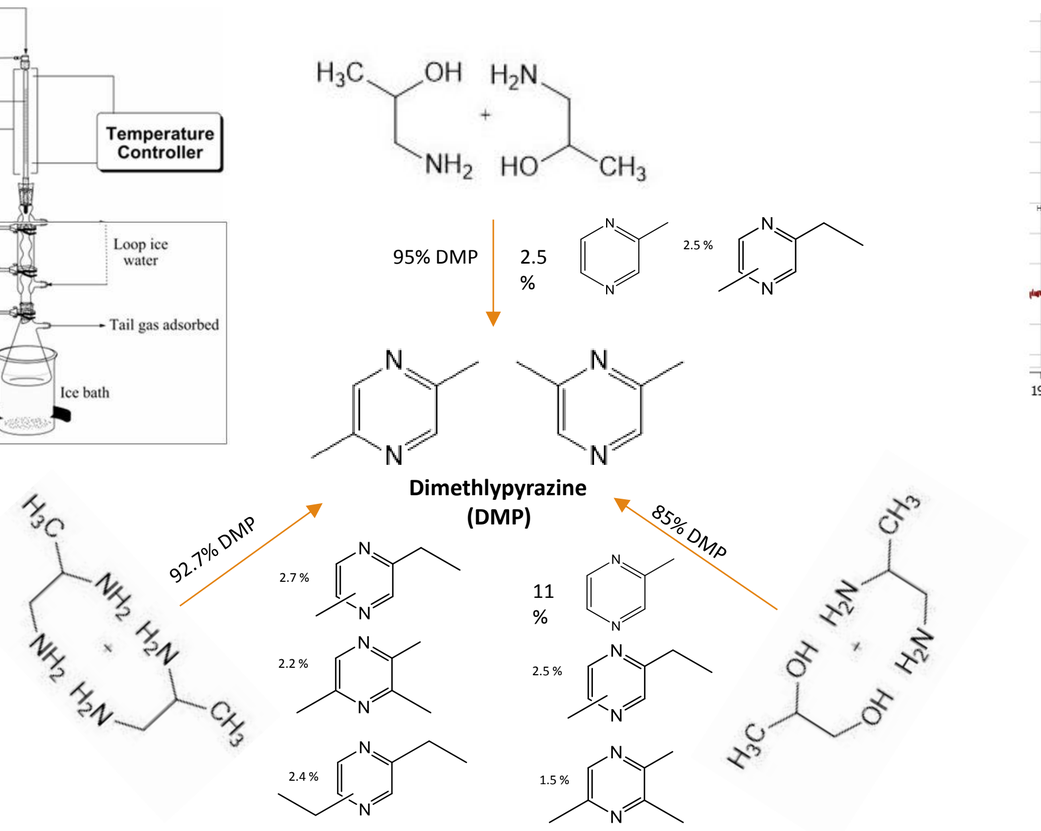
Reaction system for the synthesis of alkylpyrazines



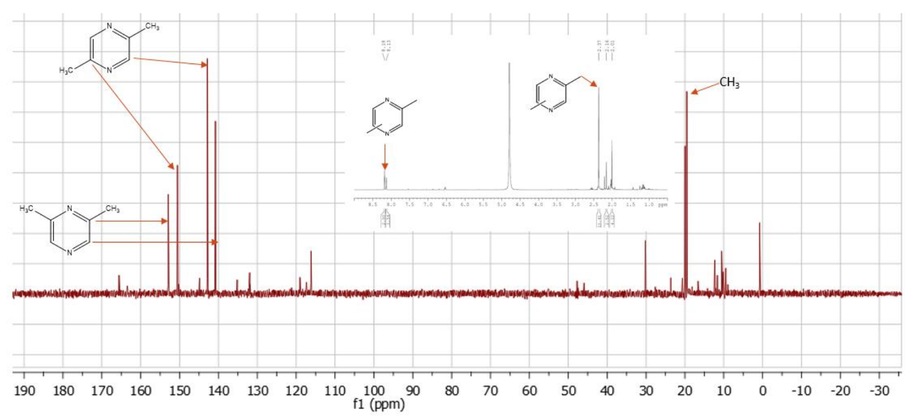
Catalyst activation: 400 ˚C, 2 h, gas mixture Ar:H_2 = 1:1 (vol.), gas flow rate = 20 mL/min, t = 2 h;

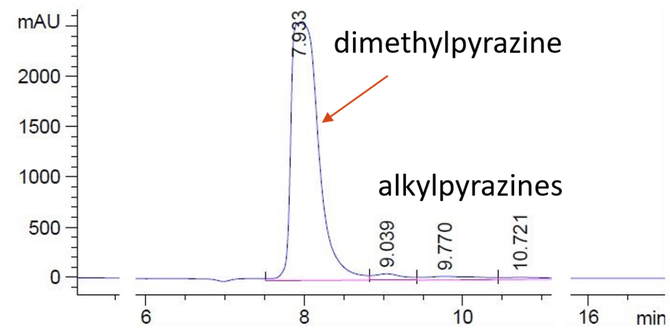
Reaction: 400 ˚C, reactant mixture 50% water (vol.), reactant flow rate = 1 mL/h, Ar carrier gas, gas flow rate = 10 mL/min.

DMP synthesis *via* 3 types of cyclo-dehydrogenation reactions



NMR spectra and HPLC analysis of 2,5 and 2,6 DMP





Conclusions

- mo-Zn/Al obtained from a LDH type material has presented a very good activity for obtaining alkylpyrazines from different raw materials, making it suitable for studying the influence of different moieties in the cyclo-dehydrogenation reaction;
- The acid sites on the catalyst are facilitating the cracking of raw materials containing primary alcohol groups (vicinal diols), which leads to an increase in lower carbon secondary products;
- The reactions between diamines afford only small quantities of superior alkylpyrazines as secondary products; the C-N bond in the raw materials can undergo hydrogenolysis, affording low-boiling compounds that can alkylate the pyrazines previously formed on the catalytic bed;
- The 3 types of cyclo-dehydrogenation reactions are appropriate for obtaining a wide variety of alkylpyrazines.

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