Catalytic synthesis of alkylpyrazines over mixed oxides obtained from LDHs materials

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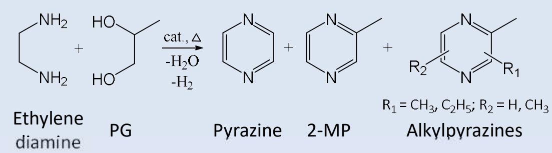
Introduction

Alkylpyrazines are a class of N-heterocyclic compounds often found in the composition of natural and synthetic compounds. Consequently, there are numerous alkylpyrazines applications in the industrial area (e.g. food, agriculture and pharmaceutics).
Because of the wide variety of applications, alkylpyrazines synthesis is a continuous goal of chemistry. The coupling reactions assisted metal-catalyst is one of the most effective synthesis route, involving an Eley-Rideal mechanism on a bifunctional catalyst. In this context, mixed oxides obtained from layered double hydroxides (LDHs) were evaluated as catalysts in alkylpyrazines synthesis by dehydration-cyclization of 1,2 diamines with propylene glycol (PG), followed by the dehydrogenation of the obtained pyperazine. Considering the large interest for alkylpyrazines, finding new materials able to catalyze these reactions is still a challenge.

Results and discussions

General reaction scheme for 2-methylpyrazine (2-MP) synthesis



LDHs materials with a $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}]\cdot mH_2O$ general formula

where M^{2+} = Zn, Co, Ni and M^{3+} = Al

M^{2+}/M^{3+} molar ratio of 3

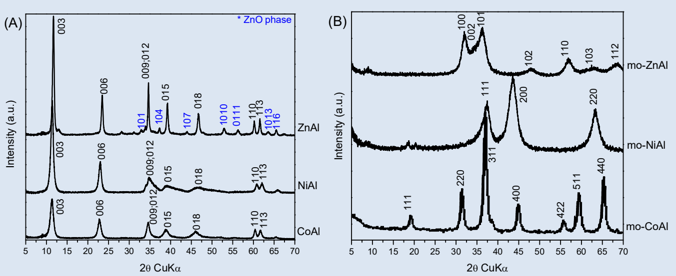


Fig. 1. The XRD patterns of samples (A – layered double hydroxides; B – mixed oxides obtained by calcination of LDH)

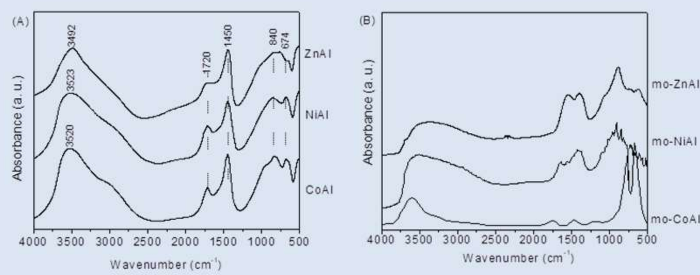


Fig. 2. DRIFT spectra of samples (A – layered double hydroxides; B – mixed oxides obtained by calcination of LDH)

- The catalytic activity measurements were carried out at atmosphere pressure in a fixed-bed down-flow integral reactor at 300-400 °C

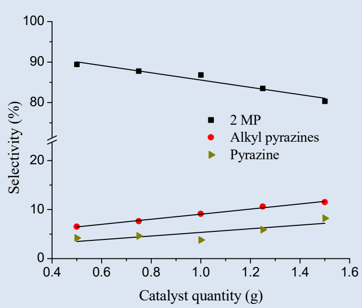


Fig. 3. Influence of catalyst loading on pyrazines selectivity (mo-ZnAl, T = 400 °C, flow rate 1 ml h^{-1})

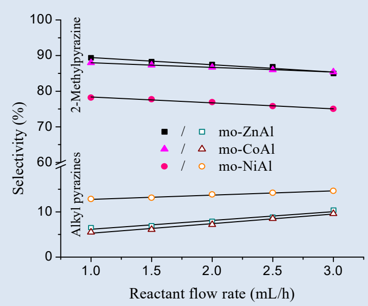


Fig. 4. Influence of the reactant flow rate on pyrazines selectivity (T = 400 °C, over 0.5 g of catalyst)

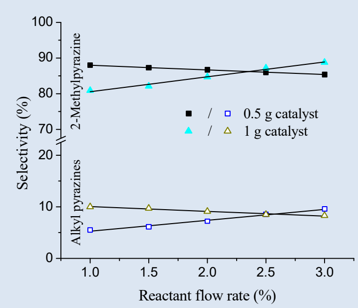


Fig. 5. Influence of the reactant flow rate on pyrazines selectivity (over different CoAl catalyst loadings)

Conclusions

- Layered catalytic materials were obtained by mechanochemical route, this being a facile and economic route. The layered structure has been demonstrated by X-ray diffraction and DRIFT;
- Mixed oxides obtained from layered double hydroxides (LDHs) present the ditopic character having acid and base sites necessary for in alkylpyrazines synthesis;
- There is a significant influence in the conversion and selectivity values offered by the type of cation used, the reaction temperature, catalyst loading, flow rate of the reactants;
- The materials are thermally stable and the catalytic sites can be regenerated after they are reduced with hydrogen under controlled conditions.

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