

## Acid sites requirements in the gas phase methylation of imidazole

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### Introduction

The N-alkylation of heterocyclic compounds, such as imidazole or pirazole, is a useful reaction for the preparation of fungicidal, anticonvulsant, bactericidal and protozoacidal drugs. 1-Methylimidazole, in particular, can be used as cocatalyst for the synthesis of cyclic carbonates from carbon dioxide and epoxides, also as raw material in the manufacturing of ionic liquids, which can replace conventional solvents for catalytic and organic reactions.

The gas phase methylation of imidazole has been studied on acid zeolites such as HY, HZSM5 and HMOR and mixed oxides of Al and Mg. However, further analysis of the reaction including the identification of the catalytic active sites and catalyst stability is still required.

The aim of our work was to elucidate the nature and strength of the catalytic acid sites involved in the N-alkylation of imidazole.

Imidazole                      N-Methylimidazole

Figura 1. Reaction Scheme

### Experimental

The catalysts employed in this work were: zeolites HBEA (Zeocat PB/H), HY and ZnY (obtained by ion exchange of commercial NaY,UOP-Y); HMCM22 synthesized in our lab, HPA/SiO<sub>2</sub> prepared by wet impregnation. The strength, density and nature of the acid sites were determined by NH<sub>3</sub> TPD and FTIR using pyridine as a probe molecule. The gas phase alkylation reaction was carried out at 523 K in a fixed bed by feeding a solution of Imidazole (IMI)-Methanol (M) with a molar ratio M/IMI=10.

### Results y Discussion

The densities of surface acid sites were determined by integration of NH<sub>3</sub> TPD traces and are displayed in Table 1.

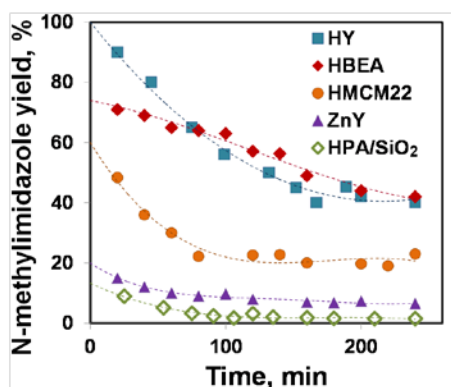
The catalysts based on Y zeolite (ZnY and HY) exhibited the greatest concentrations of acid sites. The acid strength of HPA/SiO<sub>2</sub> was clearly higher with a desorption peak at 900 K (TPD profile not shown here) but the acid sites density per gram was the

lowest. HY and HBEA zeolites showed a similar contribution of both Brønsted and Lewis acidity. The incorporation of Zn<sup>2+</sup> in the Y zeolite generated essentially strong Lewis sites that after evacuation at 573 K retained 75% of pyridine remaining after evacuation at 423 K (Table1). The acidity of HPA/SiO<sub>2</sub> and HMCM22 was predominantly Brønsted, with a Brønsted/Lewis (B/L) ratio of 6 and 3 (T<sub>des</sub>=423 K)

**Table 1:** Sample acidity

Catalyst	TPD NH <sub>3</sub> μmol/g	IR of pyridine			
		T <sub>desorption</sub> =423K		T <sub>desorption</sub> =573K	
		Brønsted sites	Lewis sites	Brønsted sites	Lewis sites
HY	1430	310	465	209	177
ZnY	2121	37	1200	9	880
HBEA	556	150	151	74	92
HMCM22	470	560	176	444	120
HPA/SiO <sub>2</sub>	160	91	15	70 <sup>‡</sup>	10 <sup>‡</sup>

<sup>‡</sup>T<sub>desorption</sub>=473K



**Figure 2:** N-Methylimidazole yield as a function of time on stream.

and HMCM22 (Figure 2 and Table1). Solids that have strong acid sites of Lewis or Brønsted nature almost exclusively were less active. Indeed, the yields at t=0 h on ZnY and HPA/SiO<sub>2</sub>, obtained by extrapolating the respective curves to the origin, were 20% and 14% respectively. On zeolites HY and HBEA, which have B/L ratio closed to 1, the highest yields at t=0h (100% and 74%) were obtained, denoting that the simultaneous presence of Brønsted and Lewis acid sites promoted efficiently the N-alkylation reaction.

The catalytic results are presented in Figure 2 where N-methylimidazole yield is plotted as a function of time on stream. The selectivity to the desired product was always higher than 95%. It is noteworthy that all catalysts deactivated during the course of the reaction, although it was more significant on catalysts which possess higher density of strong Brønsted acid sites such as HY