

A systematic study of isomorphically substituted H-MeAlPO-5 materials for the Methanol to Hydrocarbons (MTH) reaction

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Abstract: Careful design and rigorous execution of the synthesis of a consistent series of isomorphically substituted H-MeAlPO-5 materials allowed us to unambiguously attribute the observed differences in catalytic performance to acid strength associated with the modified BAS. All materials were shown to be active in MTH at 450 °C with clear activity differences, agreeing well with the predicted acid strength. The materials exhibit clear selectivity differences. Strong acids (Mg, Co, Zn), show the highest selectivity towards the desired alkene products, while medium strength acid (Si) shows an increased selectivity towards aromatics and alkanes while diminishing the proportion of alkenes.

Keywords: Microporous materials, Methanol to hydrocarbons, Solid acid catalysis.

1. Introduction

The conversion of methanol to hydrocarbons (MTH) represents a family of flexible processes for production of a variety of hydrocarbons¹. The reaction proceeds over Brønsted acidic zeolite and zeotype materials, where methanol or DME is converted through a complex network of reactions, referred to as the hydrocarbon pool mechanism. The current mechanistic understanding, the dual cycle mechanism², divides the reaction network into general classes, namely alkene interconversion reactions and aromatic methylation and dealkylation reactions. In this work, we aim to study the effect of metal incorporation into the AlPO-5 structure and the effect of the created BAS on the MTH reaction. The synthesized materials span a wide range of acid strengths and vary only in the nature of the substituted metals.

2. Experimental

A series of H-MeAlPO-5 (Me = Mg, Co, Zn, Si, Zr, Ti) were synthesized hydrothermally, characterized with XRD, SEM, EDS, N₂ adsorption, *n*-propylamine TPD and FT-IR. NH₃ adsorption energy was calculated using BEEF-vdw density functional. The materials were tested in the MTH reaction in a quartz fixed bed flow reactor at 450 °C using DME as feed. The reaction effluent was analyzed with an online GC-MS.

3. Results and discussion

A set of highly crystalline metal substituted AlPO-5 materials were successfully synthesized hydrothermally (Table 1).

Table 1 Key material characteristics for synthesized H-MeAlPO-5 materials

Material	Crystal Size (μm)	BET (m ² /g)	Acid site density (mmol/g) ^a	Density of Me (mmol/g) ^b	ΔE _{NH₃} (kJ/mol)
H-MgAlPO-5	1 x 2.5	360	0.102	0.1	-128
H-ZnAlPO-5	1 x 2.5	362	0.094	0.2	-121
H-CoAlPO-5	1.5 x 2	347	0.081	0.2	-119
H-SAPO-5 ^c	1 x 2	340	0.068	0.3	-83

H-ZrAlPO-5	2 x 4.5	352	0.065	- ^d	-75
H-TiAlPO-5	3.5 x 3	329	0.060	0.2	-75
AlPO-5	1 x 1	370	n.a.	- ^e	-

^aDetermined by *n*-propylamine TPD ^bEstimated from EDS, based on ratio of Me and either Al or P ^cSee ref 3 ^dOverlap between Zr/P peaks, no estimate obtained. ^eNo heteroatom detected by EDS.

The materials form a series with similar key properties such as particle size, morphology, surface area and acid site density, making them well suited for a single-parameter study of the catalytic properties of the created Brønsted acid site. All synthesized H-MeAlPO-5 materials were tested as catalysts in the MTH reaction at 450 °C to evaluate catalytic activity. The tests showed that the three predicted stronger acids (Mg, Co, Zn) were significantly more active than the medium acidic H-SAPO-5 and the weaker acids (Zr, Ti), with turn-over frequencies spanning an order of magnitude. Furthermore, metal substitution was found to influence product selectivity. The stronger Brønsted acids (Mg, Co, Zn) produced more alkenes (propene in particular), compared to the medium acidic and weakly acidic materials (Si, Zr) (Figure 1). Conversely, H-SAPO-5 and H-ZrAlPO-5 showed higher selectivity towards aromatics and alkanes compared to H-MgAlPO-5, H-CoAlPO-5 and H-ZnAlPO-5.

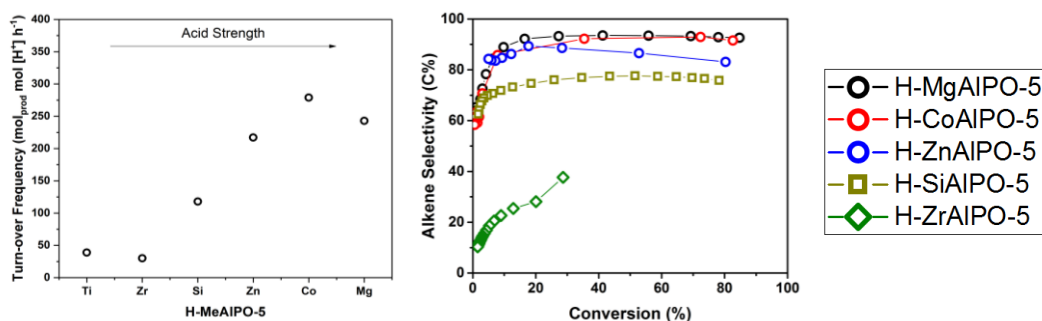


Figure 1. Turn-over frequency in MTH reaction over H-MeAlPO-5 materials (left) and product selectivity to alkenes (C₂, C₃, C₄, C₅ and C₆₊) (right) at 450 °C.

These results show that isomorphic substitution of metals into the framework alters both the activity of the acid site and the relative rates of different classes of reactions, suggesting that methylation and cracking reactions forming light alkenes dominate the strongly acidic materials. The influence of isomorphic substitution on individual reactions steps in MTH is currently in progress in our labs.

4. Conclusions

A series of metal-substituted aluminophosphates with AFI topology that differ in acid strength and span a predicted range from high to low Brønsted acidity was synthesized. The synthesis was aimed to produce materials with homogenous properties in order to isolate the influence of metal substitution. The materials were tested in the MTH reaction at 450 °C using dimethyl ether (DME) as feed. A clear activity difference was found, where the predicted stronger acids converted DME significantly faster than the medium and weak Brønsted acidic materials. The stronger acids produced more alkenes than the weaker acids at the expense of aromatics and alkanes.

References

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