CATALYTIC CONVERSION PROCESS OF METHANOL-TO PROPYLENE (MTP) WITH ZEOLITES

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ABSTRACT

Zeolites HSZM5 and HMOR are synthesized and analyzed their behavior in the conversion to propylene from methanol (MTP). These zeolites were studied with XRD and was established that acidity is a parameter that influences the processes of conversion of methanol to propylene.
Keywords: Conversion methanol, HMOR, HZSM5, MPT.

INTRODUCTION

Mordenite is a zeolite with orthorhombic structure with the dimensions of a unit cell[1-5] of: a ¼ 18:13) b ¼ 29:49) c ¼ 7:52). The fact that the mordenite presents a Si/Al molar ratio ≥5, makes it very resistant to severe thermal and chemical treatments. With a Si/Al molar ratio equal to 5 the completely hydrated sodium form has the ideal composition of $Na_8Al_8Si_{40}O_{96}.24H_2O$[1-10]. This work shows the effects catalytic of HMOR and HZSM-5 in the conversion of methanol to propylene and selectivity and its results are compared with other reported in the literature[11-17].

EXPERIMENTAL

The ZSM5 and HMOR were prepared according to literature. The methanol conversion was carried out in a fixed bed reactor at 450 ˚C under atmospheric pressure. Prior to each reaction, the samples (0.5 g) were pretreated in He flow at 550 ˚C for 2 h and cooled to a reaction temperature. Methanol (Sigma-Aldrich, C99.9%) was fed into a reactor by a liquid mass flow controller (Bronkhorst High-Tech, LIQUID-FLOW series L10/L20) and the weight hourly space velocity (WHSV) was 2.88 h^{-1}. A homogeneous mixture of MeOH (10%) and He (90%) was achieved by using a pre-heater to vaporize the methanol. All products were passed through a heated transfer line to a gas chromatograph with a thermal conductivity detector and a flame ionization detector (column: HP-PLOT Q, Agilent) in series.

RESULTS AND DISCUSSION

Methanol conversions as well as selectivity's (product distribution) of the catalysts synthesized, HZSM5 and HMOR are presented in Table-1 for the pure HZSM-5 (SiO_2/Al_2O_3 = 80), selectivity to C1–C4 saturated hydrocarbon, ethylene, propylene and butylene was 18.5, 18.0, 22, 7 and 8.25 C mol%, respectively. Compared with HZSM-5, the propylene selectivity of the HMOR catalyst was of double while the C1–C4 saturated hydrocarbon selectivity increased and the butylene selectivity decreased. The changes in product distribution must be due to the major acidity of the HMOR catalyst, the propylene and butylene selectivity dramatically increased to 44.2 and 19.4 C mol%, respectively, while the C1–C4 saturated hydrocarbon decreased to 3.62 C mol% due to the decrease in strong acidity as well as the weakening of strong acid strength. The well-known methanol conversion consists of three main reaction steps. Methanol is dehydrated to dimethylether and the equilibrium mixture formed, consisting of

methanol, dimethylether and water, undergoes further dehydration to produce light olefins. The subsequent conversion of light olefins to paraffins, aromatics, naphthenes and higher olefins occurs.

Table -1: MTP reaction over unmodified and mesopore-modified HZSM-5 catalysts[c]

Catalyst	Conv. (%)	Selectivity (C-mol%)						P/E
		C_1–C_4[a]	C_2H_4	C_3H_6	C_4H_8	C_5[b]	Aromatics	
HZSM5	99.6	18.5	18.0	22.7	8.25	12.6	20.0	1.75
HMOR	99.8	3.62	6.88	44.2	19.4	23.9	2.60	10.1

[a] C_1–C_4 saturated hydrocarbons.
[b] C_5 and higher hydrocarbons excluding aromatics.
[c] Reaction conditions: T=470 °C, WHSV = 1 h^{-1}, P_{CH3OH}=0.5 atm, H_2O:CH_3OH = 1:1.

The propylene selectivity is affected by the Brønsted acidity of catalyst and there is an optimum Brønsted acidity of catalyst for the high propylene selectivity. In the case of HZSM-5 without Brønsted acidity, methanol was not converted to hydrocarbon and main product was dimethylether[16]. The changes in product selectivities with time on stream for HMOR as of representative catalyst are presented in figure-1.
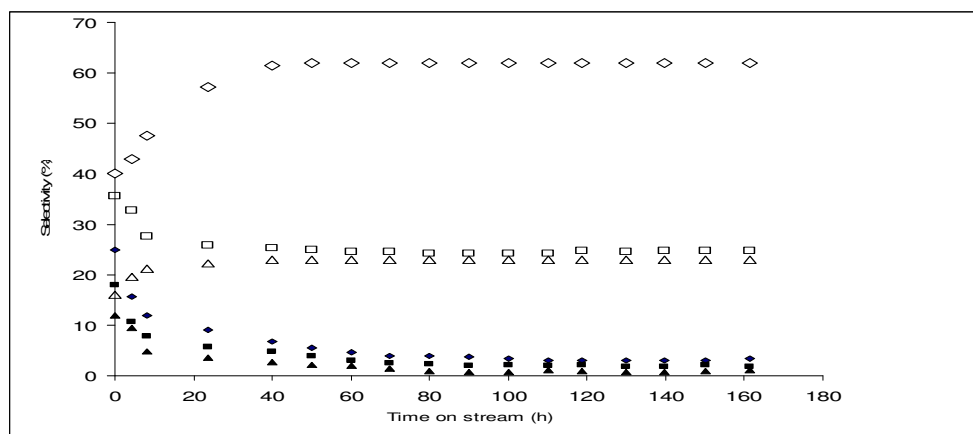

Fig.-1: Product selectivity of HMOR as a representative catalyst for MTP reaction as a function of time: (◊) C_3H_6; (■) C_2H_4; (Δ) C_4H_8; (▲) aromatics; (♦) C_1–C_4 saturated hydrocarbons; (□) C_5 and higher hydrocarbons excluding aromatics. Reaction conditions: T=470 °C, WHSV=1h^{-1}, P_{CH3OH}=0.5 atm., H_2O:CH_3OH = 1:1.

CONCLUSION
In this work we synthesized of zeolites type HMOR and HZSM5. The HMOR is more effectively convert methanol to propylene that HZSM-5. This effectively is associated to a different content of acid groups. This work shows novel results for this type reaction and more yield.

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