

Catalytic Activity of MEL Zeolites Modified with Metallic Couples for the Conversion of Ethane

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Abstract: The transformation of ethane into aromatic hydrocarbons over Zn-metal- containing zeolites at W/F=10 gh/mol and 550°C was studied in a flow reactor at atmospheric pressure. Zn-metal-zeolite modified the activation mode of the alkane, generating highly reactive intermediates and enhancing the aromatic selectivity.

Introduction

The transformation of light alkanes into more valuable compounds, such as aromatic hydrocarbons (AH), is of great importance from both the industrial and academic points of view. MEL and MFI zeolites loaded with metal cations, such as zinc and molybdenum have been successfully used for this purpose showing very pronounced selectivity for aromatic hydrocarbons [1-6]. At the moment, the utilization of zeolites modified with metallic couples for the paraffin conversion has not been reported. Here we discuss the catalytic behavior of MEL zeolites modified with Zn-metal couples in the activation of ethane and suggest a relation between structure - activity.

Experimental

Zeolites with a Si/Al molar ratio of 17 were synthesized by hydrothermal crystallization in Na₂O-Al₂O₃-SiO₂ systems, in the presence of tetrabutylammonium hydroxide as template agent. The cations were incorporated by ion exchange of NH₄-zeolite except the molybdenum, which was incorporated by incipient impregnation. Catalytic reactions were carried out in a continuous flow quartz reactor at atmospheric pressure. Products were withdrawn periodically from the outlet of the reactor and analyzed by an on-line gas chromatograph equipped with a FID detector. Conversion and products distribution were expressed on a carbon-atom basis.

Results and Discussion

Table 1 shows the results of catalytic activity of acidic and Zn-metal- containing zeolites for ethane

transformation. The ethane conversion is very low over the protonic form of ZSM-11. The metal species loading improved the conversion of ethane as well as the selectivity to aromatics.

Table 1. Ethane conversion and reaction products selectivity over various catalysts at 550°C, W/F= 10 gh/mol, total pressure of 1 atm and TOS= 20min.

Catalyst	Conversion mol % (C)	Selectivity, mol % (C)			
		C1	C2=	C3-C5	AH
H-ZSM-11	1.5	29.3	46.7	7.3	16.7
Zn-ZSM-11	11.26	2.44	54.74	9.10	33.72
ZnPb-ZSM-11	8.24	2.82	43.05	8.59	45.54
ZnMo-ZSM-11	12.34	5.47	40.08	8.38	46.05
ZnCu-ZSM-11	5.72	1.68	59.03	7.69	31.60

FT-IR data for chemisorbed pyridine after adsorption at room temperature and after further outgassing the samples at 250, 350 and 400°C indicate that the number and strength of Lewis sites increases by incorporation of metal cations into the zeolite. Zn-metal-ZSM-11 could act as a hydride abstractor in the ethane activation and the function of metal species would be the dehydrogenation of ethane into ethylene and of the naphthenic intermediates into aromatics [3,5].

Conclusions

MEL zeolites modified with metallic couples are effective for the activation and aromatization of ethane. The first step would be the direct abstraction of a hydride from ethane, producing a ethyl-carbenium surface ion through the electron-donor acceptor adduct (EDA) formation, and then by deprotonation ethylene. Ethylene would undergo secondary transformations toward the aromatization.

References and Notes

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