

Catalytic Naphtha Cracking

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Introduction

Demand growth for ethylene and propylene as primary petrochemicals have been high at 5 and 6%, respectively and these trends are expected to continue in the future. Most of ethylene is made thermally by steam cracking of naphtha at high temperatures. This leads to large amounts of undesirable by-products, which include methane, highly unsaturated olefins, and fuel oil. Also, thermal cracking through radicals is governed by Beta scission reaction pathways which favor ethylene formation over propylene. There is a need to develop a relatively low temperature catalytic naphtha cracking process with less by-products formation and with higher propylene selectivity in order to meet the higher demand for propylene.

Materials and Methods

A series of 8-, 10- and 12-membered ring zeolites (in H-form) were synthesized and evaluated for cracking naphtha (Table 1) in a fixed bed reactor at temperatures much lower than those used for steam cracking operation.

Results and Discussion

Zeolites possess active sites that enable selective cracking of alkanes and naphthenes into ethylene and propylene through primary and secondary reaction pathways. Activation is presumably occurring through direct protonation to generate the carbonium ion, which then splits into a lighter alkane and a carbenium ion or into hydrogen and a carbenium ion. The primary reaction products --alkanes and the alkenes-- that result from deprotonation of the carbenium ions can undergo secondary cracking, aromatization and hydrogen transfer reactions. Shape selectivity effects, crystal morphology, as well as acid site density characteristics govern the occurrence of various steps, from introduction of the reactant molecules into the zeolite pores, to splitting of the carbonium ion, to the regulation of the secondary reactions and to the gradual deactivation of sites. Coking is the primary deactivation mechanism. A regeneration step restores the zeolite's ability for selective cracking in a subsequent process cycle.

A range of zeolitic catalysts were tested for cracking naphtha (Tables 2 and 3). Due to their relatively larger kinetic diameter, isoalkanes and naphthenes exhibited lower reactivity than linear alkanes over 8-MR zeolites. 12-MR zeolites, for example Beta, were more prone for enabling bimolecular hydrogen transfer reactions, which increased the selectivity to light alkanes and to coke at the expense of ethylene and propylene. Hydrogen transfer was controlled by keeping the number of acid sites at a minimum. Primary reaction products n-butenes/n-butane showed low reactivity over 12-MR zeolites, ie. Y-zeolite. The highest ethylene and propylene yields were obtained over 10-MR zeolites, ie. Ferrierite. This chemistry provides the potential for developing an improved naphtha cracking process that is more selective to ethylene and propylene relative to steam cracking.

Table 1: Composition of Naphtha Feed (by wt-%)

Carbon	<4	5	6	7	8	9	>10
<i>n</i> -alkanes	0.9	11.0	5.5	3.1	2.6		
<i>i</i> -alkanes		12.1	8.3	3.4	2.6		
naphthenes			7.1	7.7	4.7		
Aromatics			0.9	1.8	4.6	3.5	2.2
undetermined			0.1	0.1	0.8	10.6	6.4
Total	0.9	23.1	21.9	16.1	15.3	14.1	8.6

**Table 2: Conversions for Different Feed Components over Zeolites
6 g catalyst, 0.15 g naphtha, 1-2 sec, 1-3 N₂ :feed (molar), 650 C, 4 psig**

	Si/Al ₂	Naphtha	<i>n</i> -C ₅	<i>i</i> -C ₅	Cyclohexane
Y	81	85	53	77	93
Beta	66	85	76	84	90
ZSM-22	62	85	98	91	98
ZSM-23	89	85	100	87	80
Ferrierite	71	85	93	77	81
ZSM-35	19	85	99	73	45
EU-1	70	85	93	94	92

Table 3: Selectivities (by wt-%) at 85% Naphtha Conversion

	C ₁	C ₂	C ₂₌	C ₃	C ₃₌	C ₄ /C ₄₌	Aromatics	H ₂	Coke
Y	9	4	16	5	30	16	12	2	6
Beta	9	6	17	15	18	10	13	2	10
ZSM-22	7	7	26	5	27	8	16	1	3
ZSM-23	8	8	27	4	26	7	17	1	2
Ferrierite	6	7	28	3	31	9	11	1	4
ZSM-35	11	8	24	2	21	6	15	2	11
EU-1	9	6	21	10	20	6	18	2	8

