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## 1. Introduction

Catalytic cracking is the most important process in a modern oil refinery. Hydrocarbon C-C bonds present in the feedstock, usually vacuum gas oils or residues, are broken in order to obtain gasoline and light alkenes. The active component of the catalyst is Y-type zeolite. However, ZSM-5 can be added to increase the yield of propylene.

**Objective of this research:** develop a kinetic model that can account for the influence of the catalyst properties of FAU and MFI zeolites on activity and selectivity

## 3. Kinetic model

Single event microkinetic model for catalytic cracking of hydrocarbons on zeolites.

A limited number of catalyst descriptors to account for the influence of acidity and framework topology:

- number of active sites of the catalyst
- change in protonation enthalpy
- change in activation energy
- physisorption properties of the catalyst

## 2. Experimental

A series of five (US)Y and three ZSM-5 zeolites differing in acid characteristics have been tested. Cracking experiments have been performed in a recycle electrobalance reactor set-up equipped with online GC analysis.

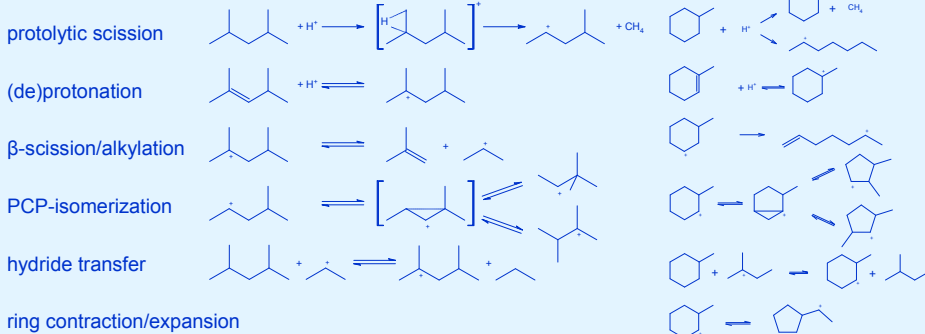
model components: 2,2,4-trimethylpentane CC(C)C(C)C, methylcyclohexane CC1CCCCC1

operating conditions: temperature 425-490 °C, partial pressure 3-15 kPa, space time 8-215 kg.s/mol

Catalyst		Si/Al bulk	Si/Al frame	mol NH <sub>3</sub> /kg
LZ-Y20	H-USY	2,6	30,0	0,99
Y62	NH <sub>4</sub> -Y	2,6	2,6	3,49
CBV 500	NH <sub>4</sub> -USY	2,6	3,9	1,50
CBV 720	H-USY	15	16,0	0,60
CBV 760	H-USY	30	100	0,23
CBV 3020 <sup>E</sup>	H-ZSM-5	15	18,4	?
CBV 5524 <sup>G</sup>	NH <sub>4</sub> -ZSM-5	25	25,2	?
CBV 8014	NH <sub>4</sub> -ZSM-5	40	40,0	?

## 4. Results and discussion

Reaction mechanism of (cyclo)alkane cracking:

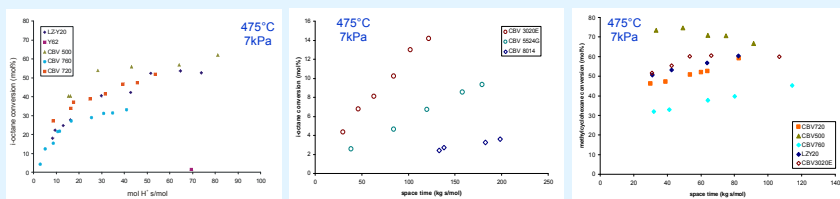


Influence of topology on product distribution:

at 15 mol% i-octane conversion

	par	ole	FAU		MFI	
C5	<chem>CC(C)CC</chem>	<chem>CC=CC</chem>	1	1	1	1
	<chem>CC(C)C</chem>	<chem>CC=C</chem>	12	3	2	1.5
	<chem>CC(C)C</chem>	<chem>CC=C</chem>	-	3	10	0.5
C4	<chem>CC(C)C</chem>	<chem>CC=C</chem>	5	23	6	5
	<chem>CC(C)C</chem>	<chem>CC=C</chem>	79	37	25	7
C3	<chem>CC(C)C</chem>	<chem>CC=C</chem>	4	32	38	39
C2	<chem>CC(C)C</chem>	<chem>CC=C</chem>	1	2	6	49
C1	CH <sub>4</sub>		7		48	

Influence of acid properties on catalyst activity:



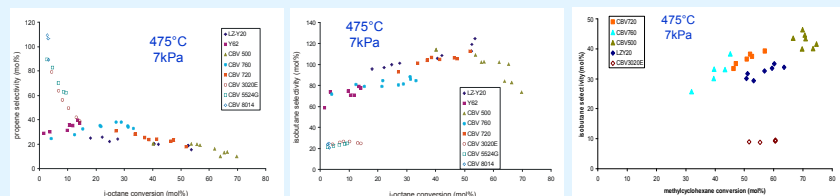
filled symbols: FAU, open symbols: MFI zeolites

at 52 mol% methylcyclohexane conversion

	par	ole	naph	aro	FAU		MFI	
C7			<chem>C1=CC=C2C=CC=CC2=C1</chem>	<chem>C1=CC=C2C=CC=CC2=C1</chem>		2		-
					6	12	0.5	11
C6	<chem>CC(C)CC</chem>	<chem>CC=CC</chem>	<chem>C1=CC=C2C=CC=CC2=C1</chem>		2	2	4	2
	<chem>CC(C)C</chem>	<chem>CC=C</chem>			13			
C5	<chem>CC(C)CC</chem>	<chem>CC=CC</chem>			1	0.5		1
	<chem>CC(C)C</chem>	<chem>CC=C</chem>			38	1		9
	<chem>CC(C)C</chem>	<chem>CC=C</chem>			5	1		7
C4	<chem>CC(C)C</chem>	<chem>CC=C</chem>			23	12		43
	<chem>CC(C)C</chem>	<chem>CC=C</chem>			5	1		5
C3	<chem>CC(C)C</chem>	<chem>CC=C</chem>			0.5	7		2
	<chem>CC(C)C</chem>	<chem>CC=C</chem>			1.5			29
C2	<chem>CC(C)C</chem>	<chem>CC=C</chem>						4
C1	CH <sub>4</sub>							

topology clearly influences product selectivities in (cyclo)alkane cracking over FAU and MFI

Influence of acid properties and topology on catalyst selectivity:



filled symbols: FAU, open symbols: MFI zeolites

## 5. Conclusions

1. The acid properties of the zeolites control the activity in (cyclo)alkane cracking, but not the selectivity.
2. The framework topology of the zeolite controls the selectivity in (cyclo)alkane cracking.
3. 2,2,4-trimethylpentane does not react inside the MFI pores, but at the external surface.
4. Methylcyclohexane cracking occurs faster than 2,2,4-trimethylpentane cracking on each zeolite tested.
5. The presence of EFAL enhances the cracking activity.