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SHAPE-SELECTIVE CRACKING OF C_8-PARAFFINS ON SILANATED H-MORDENITE

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In the cracking of C_8-paraffins mixture, silanated H-mordenite was active for the shape-selective cracking of octane with 2,2,4-trimethylpentane remaining unreacted.

Recently, much attention has been paid to the shape-selective reaction using zeolite.$^{1)}$ In principle, catalytic reactions with shape selectivity are effectively understood in the following ways: control of transport of reactant or product, and restriction of intermediate transition complexes.$^{2)}$ Zeolite pure or modified are used in these reactions, and for example, cation exchanged mordenite was used in the cracking of paraffins.$^{3)}$ In this communication, we will report on the shape-selective catalytic cracking of C_8-paraffins on silanated H-mordenite (SiHM).

Zeolite material used here was H-form mordenite (HM), supplied by Norton, 100-H. HM was first evacuated *in vacuo* at 593 K to remove the water content. To the dried HM, the vapor of $Si(OCH_3)_4$ (about 1.0 kPa) was admitted at 593 K, and the weight increase was measured *in situ* by a quartz microbalance. The HM embedded with the alkoxide was calcined in a stream of O_2 and N_2 mixture at 673 K to obtain the SiHM.

Table 1. Conversion of Cracking on HM and SiHM$^{a, b)}$

Catal	weight (mg)	Conv. (%)		Catal	weight (mg)	Conv. (%)	
		octane	2,2,4-TMP			octane	2,2,4-TMP
HM	2	11.9	2.7	SiHM	5	0	0
	5	28.9	15.6	(1.9wt%)	10	3.0	0
	10	63.7	56.6		40	63.6	0
	20	82.6	81.0		60	87.1	0
	30	84.8	77.3		100	99.3	0
SiHM	10	48.0	0	SiHM	10	0	0
(0.9wt%)	20	67.6	0	(2.8wt%)	20	0	0
	30	92.9	0		30	10.0	0
	60	100	0		40	23.4	0
					60	26.9	0
					100	63.6	0

a) Flow rate of He was 30 $cm^3 \cdot min^{-1}$. b) Average material balance was 98 %.

Catalytic cracking was performed by pulse method using helium as carrier gas in which 1 μl of a 1 : 1 ratio of octane and 2,2,4-trimethylpentane (2,2,4-TMP) mixture was injected at 573 K into the catalyst which had been pretreated at 773 K for 2 h. On HM, both paraffins were converted into lower hydrocarbons, as shown in Table 1. The ratio of octane to 2,2,4-TMP reactivity was 4.5 to 1.0 depending on the conversion. On the other hand, on the SiHM catalysts with 0.9 to 2.8 wt% loading, only octane reacted. It was noteworthy that 2,2,4-TMP did not react at all within the range of the present condition. In other words, cracking of octane proceeded selectively in the case of silanated HM.

The product distribution (Table 2) also shows discretely different trends on HM and SiHM. Branched hydrocarbons were more predominant than their corresponding normal isomers on HM, in agreement with the carbenium ion mechanism about the catalytic cracking of hydrocarbons. On the other hand, on the SiHM, the fraction of linear hydrocarbons exceeded branched hydrocarbons. Shape-selectivity was therefore observed not only in the conversion of cracking but also in the product distribution.

The present authors reported that the deposition of $Si(OCH_3)_4$ on HM reduced the pore exit size without altering the acidity.[4] The excellent shape-selectivity on the SiHM may be attributable to the transport restriction of large molecules.

Table 2. Product Distribution of Hydrocarbons in Cracking

Catal.	Conv. (%)		Product Distribution[a] (C%)[b]							
	octane	2,2,4-TMP	C_2	C_3	isoC_4	C_4	isoC_5	C_5	$C_6^{c)}$	MH[d]
HM	72.5	55.4	0.5	14.5	57.1	11.9	10.5	1.9	2.5	1.1
SiHM (0.9wt%)	48.0	0	1.2	33.9	18.2	30.3	2.2	7.5	1.8	4.7
SiHM (1.9wt%)	29.5	0	1.5	41.9	15.0	34.0	0.0	6.6	1.0	0.0

[a] Separated by liquid paraffin column operating at room temperature to 373 K. Paraffin and olefin are not separated. [b] Calculated on a carbon atom basis. [c] Mixture of C_6-hydrocarbons. [d] Methylheptane.

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