

AROMATIZATION OF C₂-C₆ ALIPHATIC HYDROCARBONS ON COPPER-CONTAINING ZSM-5 ZEOLITES

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Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

The aromatization of a wide range of model aliphatic and cycloaliphatic hydrocarbons (ethene, ethane, propene, n-hexane, 1-hexene, methylcyclopentane, cyclohexane, cyclohexene) on copper-containing NaZSM-5 and HZSM-5 zeolites has been investigated. It was established that the degree of aromatization is related to carbenium ion formation and depends on the acid strength and copper content of the zeolite. Experiments with copper-containing samples reduced prior to use indicated the possibility to enhance the selectivity to aromatization. The change of the state of Cu²⁺ ions during catalytic experiments confirmed the assumption about participation of Cu⁰ simultaneously with the Brønsted acid centers in the dehydrogenation/hydrogenation steps.

About a decade ago it was claimed that the pentasiles type of zeolites, modified with Cu²⁺, Zn²⁺ and Ga³⁺ ions¹⁻³, are able to induce aromatization of low aliphatic hydrocarbons. The industrial realization of this reaction in the processes Cyclar and M2-forming has already been reported⁴. The conversion of C₂-C₆ aliphatic hydrocarbons over Ga- and Zn-ZSM-5 was studied⁵⁻¹⁰ in detail.

The object of this work was to compare the aromatization of some low aliphatic hydrocarbons (ethene, propene, n-hexane, 1-hexene, methylcyclopentane, cyclohexane, cyclohexene) on HZSM-5 and NaZSM-5 modified with Cu²⁺ ions and to distinguish the role of the copper species and the acid centers in the aromatization steps.

EXPERIMENTAL

The initial NaZSM-5 with SiO₂/Al₂O₃ ratio 46.13 was synthesized in Czechoslovakia. The ZSM-5 structure was confirmed by XRD. The HZSM-5 form was obtained by treating NaZSM-5 with 0.6M-HCl (24 h at room temperature). Copper was introduced into NaZSM-5 and HZSM-5 with 0.1M solution of Cu(NO₃)₂ at 355 K for 1 h (two repetitions). The composition of the catalysts was determined by AAS (Table I). The samples were characterized by EPR and ESCA measurements¹¹. The acid properties of the catalysts were

determined by TPD of ammonia in the temperature range 423 – 873 K with a heating rate of 14 K min⁻¹, using hydrogen as carrier gas (Fig. 1). The catalytic experiments were carried out in a continuous flow reactor at atmospheric pressure. The catalyst (1.5 g of zeolite mixed with 1.5 g of quartz) particles with an average size of about 1 mm were heated in air stream at 823 K for 10 h. The regeneration was done under the same conditions for 4 h. The conversions of ethene and propene were determined in the temperature range 553 – 773 K and at space velocities F/W of 60 – 480 h⁻¹; these for other hydrocarbons were: ethane 923 K, 120 h⁻¹; n-hexane 553 – 773 K, 0.5 – 1.9 h⁻¹; the other C₆-hydrocarbons 703 K, 1 h⁻¹. In some cases the CuNa- and CuHZSM-5 zeolites reduced prior to use and a mechanical mixture of 1.5 or 3% CuO and HZSM-5 were used for comparison. Aliphatic and aromatic hydrocarbons were analyzed by gas chromatography on 2 m long Porapak Q column, 2 m PEGA column and 12.5 m crosslinked silicone capillary column.

RESULTS AND DISCUSSION

At a temperature of 573 K and contact time of 120 h⁻¹ the order of catalyst activity and selectivity with respect to the aromatization of ethene and propene changes as follows:



TABLE I
Catalyst composition

Catalyst	SiO ₂ /Al ₂ O ₃	Na ₂ O, wt. %	CuO, wt. %
NaZSM-5	40.3	2.24	–
CuNaZSM-5	38.0	0.49	1.75
HZSM-5	41.0	0.22	–
CuHZSM-5	40.3	0.09	1.00

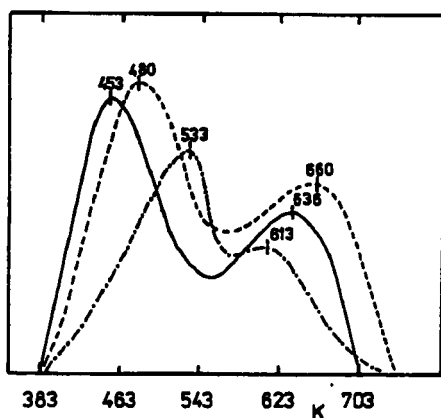


FIG. 1
Temperature programmed desorption of ammonia for zeolite catalysts HZSM-5 (—), CuHZSM-5 (---), and CuNaZSM-5 (- · - · -) (I is arbitrary intensity)

At the higher temperatures (673 and 773 K), the activity of these three catalysts becomes approximately equal. The product composition changes in a similar way for all three catalysts, with changes of reaction temperature and contact time. That is why only the results for the CuNaZSM catalyst and propene are shown in Figs 2 – 5.

The main reaction products from ethene and propene at 573 K and $F/W = 120 \text{ h}^{-1}$ (Table II, Fig. 2) are aliphatic hydrocarbons with 4, 5 and more C atoms. This indicates that the oligomerization and co-oligomerization are the predominant reactions under these conditions. As the temperature increases to 673 and 773 K, the amount of aromatics and ethane increases, and another alkane which appears is methane. At the optimal temperature for aromatization (673 K), the amount of C_3 -paraffins passes through a maximum. The low content of olefins, the absence of hydrogen and the prevailing content of paraffins suggest that the aromatization is accompanied by hydrogen transfer.

The longer contact time has a similar influence on the product distribution both for ethene and propene as have higher temperatures (Fig. 3). The optimum yields of aromatics were obtained at 673 K and $F/W = 60 \text{ h}^{-1}$. Under these conditions, the content of C_{5+} -aliphatics is minimal. This gives evidence for their role as intermediates in the aromatization process.

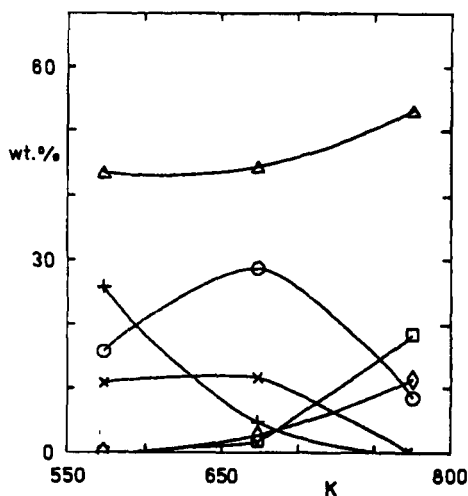


FIG. 2

Product distribution for propene transformation on CuNaZSM-5 catalyst in dependence on temperature ($F/W = 120 \text{ h}^{-1}$): methane (□), ethane (◇), propane (○), C_4 -hydrocarbons (×), C_3 - and higher hydrocarbons (+), aromatics (Δ)

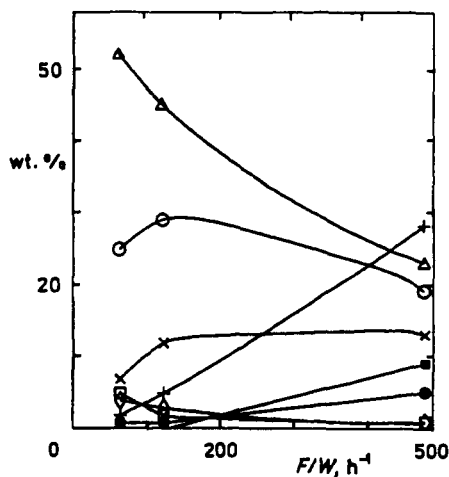


FIG. 3

Product distribution for propene transformation on CuNaZSM-5 catalyst in dependence on space velocity F/W ($T = 673 \text{ K}$): methane (□), ethane (◇), ethene (●), propane (○), propene (■), C_4 -hydrocarbons (×), C_3 - and higher hydrocarbons (+), aromatics (Δ)

The effect of reaction temperature and contact time on the distribution of aromatics in ethene and propene reaction is demonstrated in Figs 4 and 5. At 573 K, C_9 aromatics, toluene and xylenes are the main components, benzene being formed in little amount. At 673 K, benzene content increases but it still does not become the main aromatic hydrocarbon, not even at the highest temperature (773 K) and longest contact time investigated.

In the experiments with *n*-hexane (Table III), the conversion and yield of aromatics also become greater on the copper-containing samples. On the other hand, the higher aromatization ability of C_6 -cycloaliphatic hydrocarbons investigated (in comparison with that of the corresponding C_6 -alkanes) correlates well with their capability to form carbenium ions¹², as demonstrated in Table IV.

The distribution of the hydrocarbons obtained from C_6 -hydrocarbons shows that the main aliphatic components at 703 K are C_3 - and C_4 -alkanes and the main aromatics are toluene and xylenes. Hence, the product distribution in the case of C_6 -hydrocarbon aromatization is analogous to that obtained for ethene and propene reactions.

The results of our catalytic experiments are in agreement with the mechanism proposed for aromatization on Brønsted acid sites⁵⁻¹⁰ which involves the following steps: cracking, oligomerization, co-oligomerization, cyclization and dehydrogenation. The

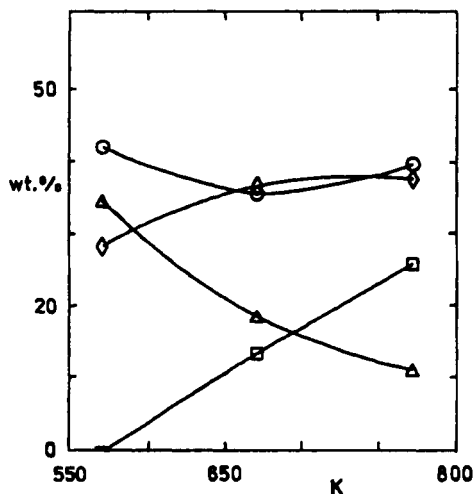


FIG. 4
Aromatics distribution for propene transformation on CuNaZSM-5 in dependence on temperature ($F/W = 120 \text{ h}^{-1}$): benzene (\square), toluene (\diamond), xylenes (\circ), C_9 - and higher hydrocarbons (Δ)

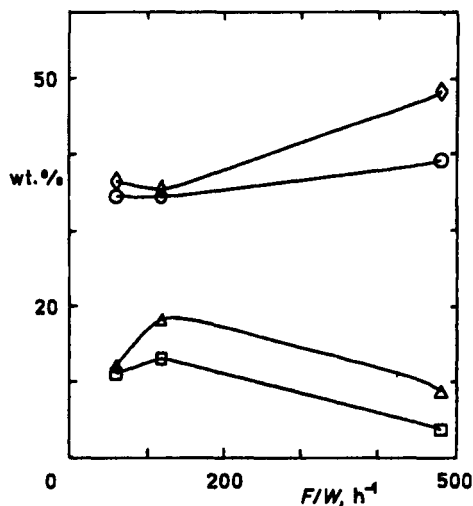


FIG. 5
Aromatics distribution for propene transformation on CuNaZSM-5 in dependence on space velocity F/W ($T = 673 \text{ K}$). For compounds designation see Fig. 4

last step may proceed through hydrogen transfer from the cyclic hydrocarbons to olefins or carbenium ions.

Comparison of the yield of aromatics, the catalyst acidity and the amount of copper introduced to the samples (Table I) demonstrates that their activity is related rather to the content of copper cations than to the sample acidity.

The question arises at which step in the scheme proposed for the low aliphatics aromatization, one can assume the participation of the copper species.

It was suggested⁵ that Zn^{2+} cations act as strong Lewis centers at the step of the starting paraffin activation and are more effective hydride acceptors than carbenium ions. This suggestion was accepted by other authors^{9,10} for Zn^{2+} and Ga^{3+} ions. On the other side, it was assumed⁸⁻¹⁰ that gallium species activate the last step of the aromatization – transformation of cycloaliphatic hydrocarbons to aromatics. Our results support the assumption about the copper species participation in the last step of the olefin aromatization.

TABLE II

Transformations of ethene and propene on zeolite catalysts HZSM-5, CuHZSM-5 and CuNaZSM-5 (573 K, $F/W = 120 \text{ h}^{-1}$)

Quantity	HZSM-5		CuHZSM-5		CuNaZSM-5	
	Ethene	Propene	Ethene	Propene	Ethene	Propene
Conversion, %	50	87	61	90	90	98
Aromatics, % ^a	3.5	28	10	41	20	43
Product distribution, wt. %						
Methane	2	–	–	–	1	–
Ethene	35	2	31	2	6	2
Ethane	1	1	1	1	3	–
Propene	6	4	2	1	2	1
Propane	5	15	2	24	9	16
C ₄ -Aliphatics	–	11	9	12	13	11
C ₅₊ -Aliphatics	43	34	36	14	41	26
Aromatics	7	32	16	42	22	44
Aromatics distribution, wt. %						
Benzene	–	–	–	5	–	–
Toluene	13	34	6	43	18	27
Xylenes	37	37	19	38	37	40
C ₉₊ -Aromatics	50	29	75	14	45	33

^a Yield.

In the case of alkanes as starting hydrocarbons the copper species can activate the process by H^- abstraction (or by dehydrogenation) as it was already shown⁸.

It was assumed⁶ that the metal species are able to activate the starting alkenes (propene, 1-butene) and the oligomers formed in the course of the reaction through direct abstraction of H^- , followed by formation of allylic intermediates. In the case of ethene aromatization, however, the higher aromatization degree on the copper-containing catalysts cannot be explained by formation of a stable π -allyl complex. Moreover, we have not found evidence for the direct coupling of two or three allylic species, assumed⁶ for

TABLE III
Transformation of n-hexane on zeolite catalysts (653 K, $F/W = 1 \text{ h}^{-1}$)

Quantity	Catalyst			
	NaZSM-5	CuNaZSM-5	HZSM-5	CuHZSM-5
Conversion, %	6	81	68	88
Cracking products, % ^a	2.4	48	37	62
Aromatics, % ^a	–	16.5	7.6	18.5

^a Yield.

TABLE IV
Transformation of C_6 -hydrocarbons on CuNaZSM-5 (703 K, $F/W = 1 \text{ h}^{-1}$)

Quantity	n-Hexane	1-Hexene	Methylcyclo- pentane	Cyclohexane	Cyclohexene
Conversion, %	82	100	75	89	100
Cracking products, % ^a	67	59	40	50	19
Aromatics, % ^a	14	36	33	30	62
Paraffins, % ^a	66	58	39	49	18
Aromatics distribution, wt.%					
Benzene	7	6	24	13	5
Toluene	39	39	30	47	39
Xylenes	46	36	36	31	34
C_9 -Aromatics	8	11	9	9	18
C_{10} -Aromatics	–	8	–	–	4

^a Yield.

propene aromatization, i.e. benzene and C₉-alkylbenzenes are not the favored reaction products.

Another question is related to the form of the active copper species. One possibility is the participation of Cu²⁺ proposed by many authors for other cations⁵⁻⁷. The formation of Ga₂O₃ in GaHZSM-5 and their participation in the aromatization process has been discussed⁸. The possibility for CuO formation during the activation of the catalysts has been proved¹³. Under the conditions of the catalysts activation used in the present work, the formation of CuO is possible, too. Our experiments with a mechanical mixture of CuO and HZSM-5 proved the higher selectivity towards aromatization of ethene (Table V) and n-hexane (Table VI).

The last possibility is the formation of metallic copper (the so good hydrogenation/dehydrogenation agent as CuO). The experiments with the copper-containing samples reduced prior to use with hydrogen (Table VI) demonstrate their higher selectivity to n-hexane aromatization. In the course of the catalytic experiment (reduction hydrocarbon atmosphere), Cu²⁺ cations can be reduced to Cu¹⁺ and Cu⁰. There are

TABLE V

Ethene conversion and selectivity to aromatics for a mechanical mixture of 1.5% CuO + HZSM-5 (623 K, F/W = 120 h⁻¹)

Quantity	HZSM-5	1.5% CuO + HZSM-5 ^a
Conversion, %	53	88
Selectivity, %	22	38

^a See Experimental.

TABLE VI

n-Hexane conversion and selectivity to aromatics on the reduced CuNaZSM-5 and on a mechanical mixture of HZSM-5 + CuO (F/W = 1 h⁻¹).

Catalyst	Temperature, K	Conversion, %	Selectivity, %
CuNaZSM-5	703	82	17
CuNaZSM-5 ^a	703	72	26
HZSM-5	603	49	12
1.5% CuO + HZSM-5	603	58	16
3.0% CuO + HZSM-5	603	92	50

^a The sample reduced with hydrogen.

data¹⁴⁻¹⁶ for a facile reduction of Cu^{2+} in zeolites. Our ESCA and EPR studies¹¹ confirm this suggestion.

On the basis of these experiments we support the view that Cu^0 takes part in dehydrogenation steps of the aromatization, parallel to Cu^{2+} and Brønsted acid centers. Thus, on the copper-containing catalysts, the aromatization of aliphatic hydrocarbons can be considered as a bifunctional process, as reported⁵⁻¹⁰.

The higher yield of aromatics on Zn- or Ga-modifications of HZSM-5 zeolites is accompanied by the lower yield of paraffins and by the presence of hydrogen in gaseous products⁵⁻¹⁰. In our experiments, we have not found detectable amount of hydrogen, and the main gaseous components were paraffins. The reason for this fact may be participation of the copper species (in our opinion mainly Cu^0) not only in the dehydrogenation but also in the hydrogenation of alkenes, as demonstrated for Pt in the Pt/HZSM-5 catalyst¹⁷. However, participation of the strong acid centers present (Fig. 1) on the copper-containing catalysts in the hydrogen transfer process parallel with the metal species, cannot be excluded⁷.

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