CONVERSION OF METHANOL TO HYDROCARBONS OVER NATURAL MORDENITE

By

W. ZATORSKI and S. KRZYZANOWSKI
Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw

The process of methanol conversion to hydrocarbons C_1—C_5 over modified natural mordenites as catalysts was investigated. The catalysts applied show high activity but short life-time. A mechanism of the process, proceeding through methyl radical, has been proposed.

Introduction

The process of methanol conversion to hydrocarbons over zeolitic catalysts was investigated intensively in the last few years.

The development of methanol production technology from synthesis gas opens the real possibility to utilize methanol as a raw material for preparation of aliphatic and aromatic hydrocarbons.

The dehydration of methanol over zeolitic catalysts was first performed by VENUTO and LANDIS [1] ten years ago and later by TOPCHIEVA ET AL. [2]. These authors have found some amounts of light hydrocarbons in the reaction products.

H-mordenite was applied by WEBB and GATES [3] as a catalyst for methanol dehydration.

In the seventies the scientists from Mobile Research and Development Corp. [4—6] worked out the process of methanol (and other heteroorganic compounds) transformation into hydrocarbons over a new class of zeolites type ZSM. They claim high yields of C_2—C_{10} hydrocarbons and a good stability of the catalysts.

The present work has been undertaken to check the possibility of the application of natural mordenite as catalyst for the investigated process.

Experimental

Materials

Starting material for preparation of catalysts was Hungarian natural mordenite (lot No 2/76). Methanol, reagent grade, and argon or hydrogen, technical grade, were used without further purification.

Catalysts

Raw natural mordenite was treated with 4N hydrochloric acid (50 °C, 5 hrs) and afterwards washed with distilled water. The chemical composition is shown in

Table I

Chemical Composition of the Natural
Mordenite from Hungary

Chemical composition wt %	Raw mordenite	Acid treated mordenite
SiO_2	68.81	70.71
Al_2O_3	10.79	11.07
Fe_2O_3	0.82	0.51
TiO_2	0.076	0.08
CaO	2.12	1.76
MgO	0.11	0.06
Na_2O	1.84	0.80
K_2O	4.56	4.49
H_2O (1000 °C)	10.51	11.66

Table I. The cation exchange was performed by mixing the acid treated zeolite with solutions of potassium, cerium, cobalt, indium, titanium or chromium chloride at 50 °C during 7—14 days. The dried catalysts were sieved and the fraction of 0.65—1.25 mm grains was used. So obtained modified mordenites were activated in dry argon stream at the temperatures 350—500 °C. ·

Apparatus and procedure

The catalysts were tested in static and flow systems. The measurements done in static system enabled us to preselect some more promising catalysts.

The main investigations were performed in flow system. The catalytic reactor was a double U shape tube (8 mm i. d., 200 mm long). The first part of the tube was used as a preheater. The catalyst bed (10 mm deep, about 400 mg of catalyst) was placed in the second part of the reactor. Methanol vapours were carried into the reactor by argon (or sometimes by hydrogen) stream. Samples of gases from the reactor were analysed by GLC. Two types of chromatographic columns were used: 6 m long (3 mm i. d.) with a mixture of dimethylsulpholane, propylene carbonate and silver nitrate on Chromosorb P (temp. 20 °C, $p_{N_2}=2,5$ atm) and 2 m long with polyethylene glycol on chromosorb P (temp. 90 °C, $p_{N_2}=1$ atm).

Results and discussion

The products of the investigated process are mainly C_1—C_5 hydrocarbons (paraffins and olefines) and water, in some cases dimethyl ether and unreacted methanol, too.

The reaction of methanol conversion was carried out on the starting (raw) natural mordenite and on several catalysts obtained by its modification. The percen-

tage of the conversion as well as the product composition depend upon the applied catalyst, the temperatures of catalyst activation and of the reaction and the space velocity.

The catalysts were activated at temperatures between 300—500 °C. The catalytic reaction was carried out between 250 and 500 °C.

At reaction temperatures below 300 °C the conversion of methanol was rather low and the only products were dimethyl ether and water. At temperatures over 350 °C for all applied catalysts, except raw mordenite, complete (100%) conversion of methanol was observed.

The period of time between the start of the reaction and the moment of methanol appereance in the product, corresponding the complete conversion, we name catalyst "life-time".

Changes of product composition with time on stream were observed for all catalysts as are shown in Fig. 1 for the potassium exchanged mordenite. The biggest
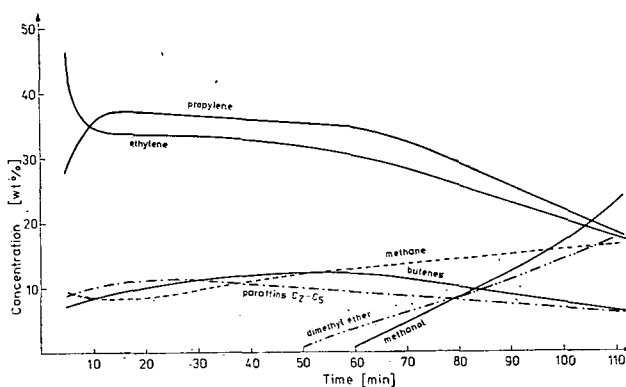

Fig. 1. Changes of product composition occuring with time on stream. Catalyst: potassium exchanged mordenite. Activation temperature: 500 °C. Reaction temperature: 450 °C. Space velocity: 0.25 g methanol/g catalyst/hr

changes of the composion take place during the first few minutes of the reaction. After that short time the catalyst activity is nearly stable. Dimethyl ether appears at the end of that period. Extending the reaction time over the value of the "life-time" one can observe the fast decrease of ethylene and propylene concentration and the rapid increase of dimethyl ether and methane contents. The "life-time" of the catalyst depends upon the type of modified mordenite. The values varied between 15 min. and 5 hrs (Table II).

The influence of reaction temperature on the process is evident. The increase of the temperature from 350 to 450 °C caused the rise of the olefine concentration and of the catalyst "life-time" (Fig. 2). Further increase to 500 °C was associated with the diminishing of the amounts of ethylene and propylene.

Table II

Natural Mordenite — Catalyzed Hydrocarbon Formation

Temperature of activation and reaction [°C]	Space velocity [g CH₃OH/g cat/hr]	Products**			
		Time of appereance [min]		Hydrocarbons [wt %] after 60 min reaction	
		Dimethyl ether	Methanol	Paraffins	Olefines
Raw natural mordenite					
350	0.31	at once	at once	18.5	35.1
400	0.31	at once	20	33.5	53.3
450	0.33	50	25	15*	84.2*
Acid treated					
350	0.24	15	60	31*	46*
400	0.34	90	100	30	70
450	0.26	150	170	26	74
Potassium exchanged					
350	0.26	110	210	41	59
400	0.29	40	20	23	60
450	0.26	300	300	22	78
Cerium exchanged					
350	0.24	60	120	39	60
400	0.30	110	120	32	68
450	0.30	150	190	22	78
Titanium exchanged					
350	0.31	20	30	30	33
400	0.35	90	150	48	52
450	0.25	135	140	40	60
Indium exchanged					
350	0.50	15	20	42*	49*
400	0.35	30	25	25	32
450	0.28	120	120	35	65
Cobalt exchanged					
350	0.27	15	15	36*	47*
400	0.29	15	30	21	48
450	0.23	40	45	26	48
Chromium exchanged					
350	0.28	15	—	30*	52
400	0.30	40	30	17	56
450	0.29	150	180	25	75

* After 30 min. of reaction.
** Without water and coke.

The temperature of catalyst activation has rather a small effect on the "life-time" of the catalyst as well as on the product composition. On the other hand, the space velocity of methanol has a great influence.

For the potassium-exchanged mordenite (Table III) the 4 times increase of space velocity decreased the "life-time" of the catalyst about 40 times. The influence was not so drastic in case of other catalysts applied. The changes of the space velocity have some effects on product composition too, especially on methane and olefine concentration (Table III).

Table III

Effect of Space Velocity on Methanol Conversion and Hydrocarbon Distributions over Potassium Exchanged Natural Mordenite

Space velocity [g CH₃OH/g catal/hr]	0.260	0.440	1.03	0.088	0.165	0.250
Temperature of activation [°C]	450	450	450	500	500	500
Temperature of reaction [°C]	450	450	450	450	450	450
Time of methanol appereance [min]	360	25	9	240	90	60

Hydrocarbon distribution [wt %] after 30 min. of the reaction						
Methane	11.0	10.3	9.7	23.0	11.0	9.8
Ethane	1.9	1.6	1.6	1.7	1.5	1.5
Ethylene	37.3	32.9	16.7	38.8	34.4	33.4
Propane	9.9	7.8	5.1	4.7	6.9	6.3
Propylene	29.5	34.3	16.1	26.0	33.2	35.9
i-Butane	2.4	1.2	0.6	1.3	1.3	1.6
n-Butane	—	0.9	0.8	0.5	1.2	0.8
Butenes	7.5	8.7	4.3	2.5	9.9	10.0
i-Pentane	0.6	0.4	0.6	0.5	0.7	0.6
Dimethyl ether	0.0	1.8	44.4	0.0	0.0	0.0
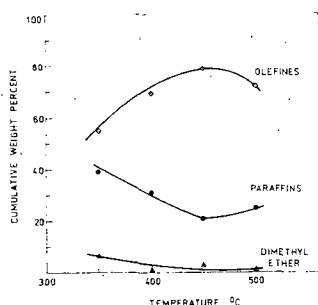
Fig. 2. Effect of the reaction temperature on the hydrocarbon distribution. Catalyst: potassium exchanged mordenite. Activation temperature: 500 °C. Space velocity: 0.26 g methanol/g catalyst/hr. Reaction time: 30 min
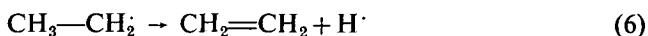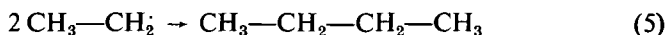
Mechanism

The mechanism of methanol-into-hydrocarbons transformation is still unknown [8]. It is obviously very complicated and proceeds *via* several steps.

We think, according to our results, that the initiating step of the process is the generation of methyl radicals occurring on radicogenic sites of the zeolite

$$CH_3OH \rightarrow CH_3^{\cdot} + OH^{\cdot} \tag{1}$$

and that methyl radicals can be the precursors of a sequence of consecutive reactions, *e.g.*:

$$CH_3^\cdot + CH_3^\cdot \rightarrow CH_3—CH_3 \tag{2}$$

$$CH_3^\cdot + CH_3—CH_3 \rightarrow CH_4 + CH_3—CH_2^\cdot \tag{3}$$

$$CH_3^\cdot + CH_3—CH_2^\cdot \rightarrow CH_3—CH_2—CH_3 \tag{4}$$

$$2\,CH_3—CH_2^\cdot \rightarrow CH_3—CH_2—CH_2—CH_3 \tag{5}$$

$$CH_3—CH_2^\cdot \rightarrow CH_2{=}CH_2 + H^\cdot \tag{6}$$

and so on.

So obtained hydrocarbons can undergo further reactions (*e.g.* cracking, isomerization, polymerization). Dimethyl ether is formed by methanol dehydration on acidic Brönsted sites of the catalysts:

$$2\,CH_3OH \rightarrow CH_3O\,CH_3 + H_2O \tag{7}$$

The water molecules, generated in the process, can modify the catalyst by formation of new acidic centers accelerating the reaction (7), leading to a decrease of catalyst selectivity.

On the other hand it is well known [9] that coke deposite formation progressively deactivates the catalysts.

Conclusions

Modified natural mordenites show catalytic activity in the process of methanol-into-hydrocarbons conversion but they undergo fast deactivation. The potassium exchanged mordenite was found to be the most interesting catalyst among the investigated samples.

The most promising aspect of the investigated process is the possibility of producing olefines from methanol.

References

[1] *Venuto, P. B., P. S. Landis:* Advan. Catal. Relat. Subj. **18**, 259 (1968).
[2] *Topchieva, K. V., A. A. Kubasov, T. V. Dao:* Vestn. Mosk. Univ., Khim. **37**, 620 (1972).
[3] *Swabb, E. A., B. C. Gates:* Ind. Eng. Chem. Fundam. **11**, No 4, 540 (1972).
[4] U. S. Pat. 3,894,106; U. S. Pat. 3,894,107; U. S. Pat. 3,928,483; U. S. Pat. 3,998,899; U. S. Pat. 4,025,571; U. S. Pat. 4,025,572.
[5] *Meisel, S. L., J. P. McCollough, C. H. Lechthaler, P. B. Weisz:* Chemtech. **6**, 86 (1976).
[6] *Wise, J. J., A. J. Silvestri:* Oil and Gas Journal, Nov. 22, (1976).
[7] *Chang, C. D., A. J. Silvestri:* J. Catal. **47**, 249 (1977).
[8] *Derouane, E. G., P. Dejaifve, J. B. Nagy, J. H. C. van Hooff, B. P. Spekman, C. Naccache, J. C. Vedrine:* C. R. Acad. Sc. Paris **284**, Série C-945, (1977).
[9] *Satterfield, C. N.:* A. J. Ch. E. J. **17**, 295 (1971).