TRANSFORMATION OF METHANOL TO HYDROCARBONS OVER Y ZEOLITES WITH VARYING Si/Al RATIO

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The catalytic activity of Na, H-Y zeolite samples with a varying Si/Al ratio (2·5 to 20) in the transformation of methanol was determined. The amounts of formed individual aliphatic hydrocarbons as function of reaction time were correlated with the amount of Brønsted and Lewis centres on the catalysts. The effect of coke formation on the over-all course of the reaction has been demonstrated.

The transformation of methanol over zeolites belongs to those reactions which have been most frequently studied lately. This was caused both by the practical importance of this process (production of light olefins and gasoline) and its theoretical interest (a deeper understanding of this complicated process and thus obtaining possibilities of influencing its selectivity). The active centres for this reaction are the acid centres of either Brønsted or Lewis type.

The most common objects of studies are ZSM-5 zeolites[1], less frequent are investigations on other zeolites with a varying pore structure[2,3]. The latter, however, are subjected to a rapid decrease in catalytic activity, caused by coke formation.

This paper deals with the results of methanol transformation over Na,H-Y zeolite samples with varying Si/Al ratio, prepared by dealumination with $SiCl_4$, as function of the time on stream and of the content of Brønsted and Lewis centres. It has been shown that coke formation in the course of the reaction affects the whole reaction mechanism.

EXPERIMENTAL

Measurements were carried out on H-Y(70) zeolite and on dealuminated forms of the original Na-Y zeolite. The dealumination was performed with $SiCl_4$. A description of both the technique of dealumination and of the samples was given previously[4]. The Si/Al ratio in the individual samples varied in the range of 2·5 to 20 (see Table I).

Prior to the conversion measurement, the zeolite samples were activated in the reactor in oxygen stream at 450°C. The methanol reaction was performed in a flow reactor with a fixed

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catalyst bed at 350°C. The amount of the catalyst was 0·4 g, the grain size 0·3—0·6 mm. The reaction mixture containing 21 vol. % methanol was prepared by saturating the carrier gas (nitrogen) with methanol vapour at 30°C. WHSV of methanol was $0·7 \, h^{-1}$. The reaction products were analyzed by gas chromatography. The light hydrocarbons $C_2 - C_5$ were separated on a 2 m long column (internal diameter of 3 mm) packed with Durapak (n-octane/Porasil C) and determined with a thermal conductivity detector. Ethane and ethylene were determined as the sum of C_2. By a separate analysis, performed in several selected cases, the total absence (or presence in traces only) of ethane in the products was established. Benzene, toluene, and methanol were determined by using a 1·5 m long column (internal diameter of 3 mm) packed with 10% tetra-β--cyanoethoxyneopentane on Chromosorb W and a flame ionisation detector. Neither benzene nor toluene have been found in the products. The concentrations of acid centres in the individual zeolite samples have been determined previously[5] and are given in Table I, together with other characteristic parameters.

RESULTS AND DISCUSSION

Methanol Transformation

In Figs 1, 2, and 3 the time courses of the activities of the samples H-Y, D and B, expressed as conversion degrees of methanol to the individual aliphatic hydrocarbons, are presented. Owing to the practically identical time course of methanol conversion to the individual hydrocarbons over samples E, D, and C, only the results obtained with sample D are shown here. The methanol conversion over the individual samples (except sample B) was 100% for 1 hour long, the conversion to aliphatic hydrocarbons remaining also constant, at about 55%. With increasing time on stream the methanol conversion decreased, attaining after about 4 h a constant value of about 75%. As at this time the methanol conversion to $C_2 - C_5$ hydrocarbons is already very low (the only products being ethylene and propylene) we suggest that the consumed amount of methanol reacts mostly to methane and to coke. Over the H-Y sample methanol conversion to ethylene decreases since the beginning of the reaction, whereas over the sample D it passes through a maximum which is attained at about 1 h time on stream. For propane the initial value over H-Y is by about 30% lower than over the sample D, after 1 h on stream the individual values near each other. The time course of propene formation passes over both samples through a maximum at about 2 h on stream, its value over H-Y being higher by about 50% when compared to sample D.

The conversion of methanol to butane and isobutane has practically the same time course over both zeolite samples. The time course of the formation of butenes is analogical to that of ethylene. The C_5 hydrocarbons are presented as their sum.

The formation of maxima on the time course curves of methanol conversion to individual hydrocarbons, as found with the samples H-Y, E, D, and C, may be interpreted by the parallel course of several reactions. We may suppose that simultaneously with the reaction of methanol to individual hydrocarbons the dimerization

TABLE I

Concentration of sodium, lattice $(Al)_s$ and total $(Al)_t$ aluminium, Brønsted (B) and Lewis (L) acid centres in the individual zeolites

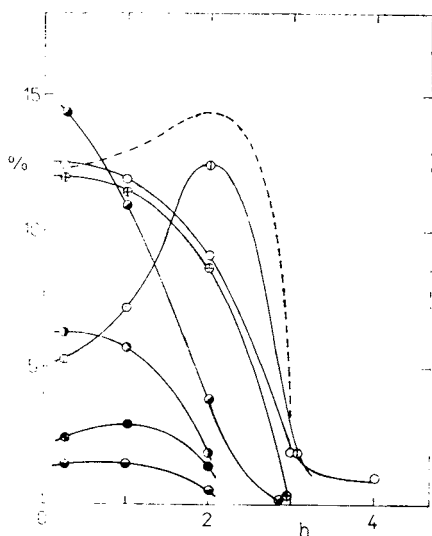| Sample	Si/Al mol. ratio	Na	$(Al)_s$	$(Al)_t$	B	L
				mmol g^{-1}		
H-Y	2·5	1·16	4·39	4·28	2·05	0·7
E	3·4	0·29	2·49	3·81	0·95	0·7
D	5·1	0·09	1·90	2·67	0·75	0·45
C	5·7	0·04	1·37	2·37	0·65	0·6
B	19·5	0·05	0·65	0·70	0·05	0·2

FIG. 1

Time course of the methanol conversion to the individual hydrocarbons $C_2 - C_5$, determined over the sample H-Y. ○ C_2H_4, ◑ C_3H_8, ◔ C_3H_6, ◓ n-C_4H_{10}, ◕ i-C_4H_{10}, ⊕ C_4H_8, ● C_5, — — — C_4H_8 (over dehydroxylated H-Y)
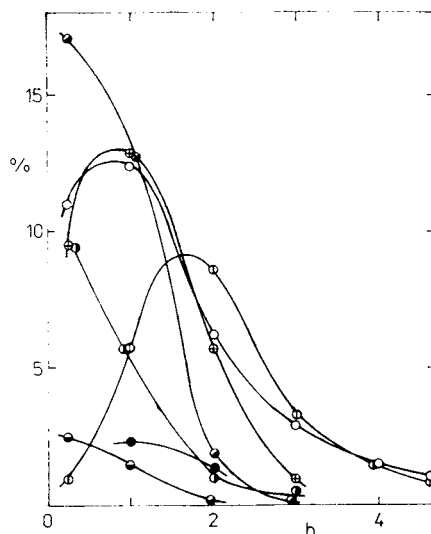
FIG. 2

Time course of the methanol conversion to the individual hydrocarbons $C_2 - C_5$, determined over the dealuminated sample D. ○ C_2H_4, ◑ C_3H_8, ◔ C_3H_6, ◓ n-C_4H_{10}, ◕ i-C_4H_{10}, ⊕ C_4H_8, ● C_5

and the oligomerization of ethylene with subsequent cracking take place, possibly also skeletal izomerization and coke formation, the latter being formed by polyene compounds with deficient hydrogen[2,6]. Although the amount of coke formed has not been directly determined, an approximate calculation was performed (based on the data given by Langner[2] for the time course of the methanol reaction to methane) leading to an amount of about 150 mg of coke, *i.e.* by about 100% higher than that given by Langner[2]. As in our case WHSV of methanol is about 3·5 times higher, both the calculated values of coke and the over-all methanol conversion values seem to be real.

By comparing the individual hydrocarbon fractions formed over samples H-Y and D at the beginning of the reaction, we find that over the dealuminated samples a higher content of paraffins is observed, whereas, on the contrary, over the sample H-Y a higher content of olefins is attained, the conversion of methanol to aliphatic hydrocarbons being practically the same over either of these catalysts. The formation of paraffins is caused by a hydrogen transfer reaction which seems to be enhanced by the presence of extra-lattice aluminium.

Measurements performed with the sample H-Y, activated at 500°C in oxygen stream for 15 h, indicate that the composition of the products of the methanol
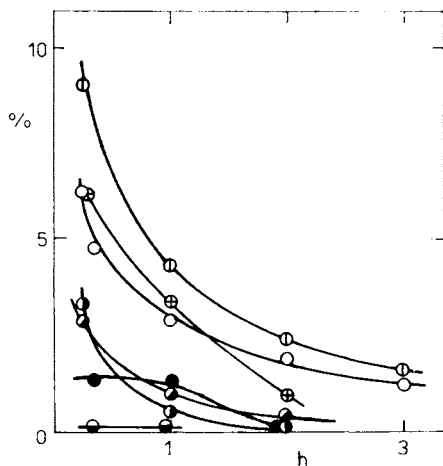
Fᴵɢ. 3

Time course of the methanol conversion to the individual hydrocarbons $C_2 - C_5$, determined over the dealuminated sample B. C_2H_4, C_3H_8, C_3H_6, n-C_4H_{10}, i-C_4H_{10}, C_4H_8, C_5
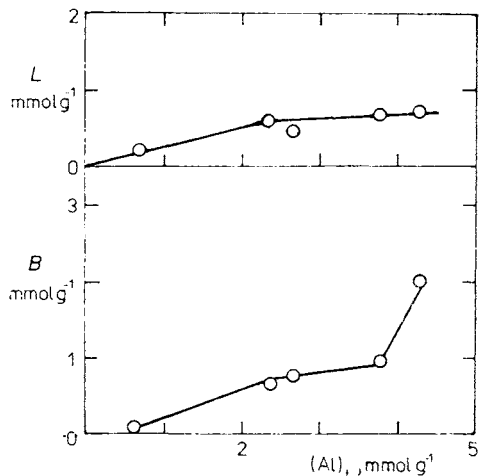
Fᴵɢ. 4

Dependence of the content (mmol g^{-1}) of the Brønsted and the Lewis centres, determined in the individual samples by the calorimetric method, on the total aluminium content $(Al)_t$

reaction is affected by the presence of Lewis acid centres. The measurements on these dehydroxylated samples show that the content of butenes is increased, this fact being evidently due to dimerization. The curve of the formation of butenes passes through a maximum after 2 h on stream and the maximum value is by 20% higher than over the original sample H-Y (Fig. 1, dashed line). With this sample, ethylene and propylene appear in the reaction products still after 5 h on stream.

After about 1 h on stream an over-all decrease of catalytic activity due to the deactivation of the catalyst by coke formation takes place and all time courses (except with propylene) have a decreasing character over both samples. In the course of the process the ratio of olefins to paraffins in the products increases by up to one order of magnitude.

The fact that the initial methanol conversion to propylene is very low, especially over dealuminated samples, seems to indicate the necessity of a certain induction period for the formation of suitable reaction conditions for the formation of propylene. The extra-lattice aluminium plays here probably a negative role.

The time course of the methanol conversion to the individual aliphatic hydrocarbons, as determined with the sample B, has a decreasing character solely. A similarity of their course to that which has been found *e.g.* with the sample D after about 2 h of methanol reaction is evident. This indicates the much lower initial activity of sample B in comparison to the dealuminated samples, possibly due to the low amount of acid centres.

The Effect of Zeolite Acidity on Selectivity

The previously determined and published[5] acidities of the investigated zeolite samples are given in Table I. In Fig. 4 the dependences of the amount of Brønsted and Lewis centres on the total aluminium content $(Al)_t$ in the zeolites are presented. Fig. 5 shows the methanol conversions to individual hydrocarbons, determined at various times on stream, as function of the total aluminium content $(Al)_t$ of the respective zeolite. Considering the fact that paraffins are formed by hydrogen transfer to the corresponding olefin, the value for the hydrocarbons in question is given as the sum of both olefin and paraffin, $\sum C_n$. From the comparison of the courses of the individual values of $\sum C_n$ in dependence on the content $(Al)_t$ it follows that (in agreement with the opinion of other authors[7]) in the initial stage of the reaction the activity of the zeolite is probably determined mainly by the Lewis centres and only after their destruction by the remaining Brønsted centres. Measurements performed over sample E after 2 h of methanol reaction support this suggestion. By argon adsorption measurements a decrease in the volume of the cavities by about 60% was found, due to coke formation. For this reason, the calorimetric curve could be determined only up to the coverage of 0.9 mmol g^{-1}. In this part of the curve, corresponding mainly to the adsorption of 1-butylamine on Brønsted centres, no changes with respect to the original curve have been found.

The dealuminated samples contain a considerable amount of extra-lattice aluminium which may act as active centres for coke formation and thus cause a more rapid decrease of the catalytic activity when compared with the sample H-Y where

TABLE II

Relative composition of butene isomers in the course of the methanol reaction, determined over a dealuminated zeolite (sample E)

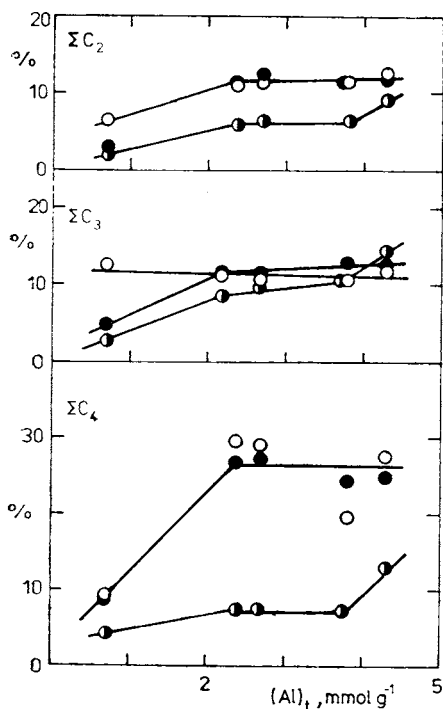| Time	1	iso	trans-2	cis-2	i/n	(i/n) $\sum C_4$
15 min	—	—	—	100	—	1·44
1 h	1·7	2·7	4·9	90·7	0·03	0·92
2 h	6·7	21·3	20·4	51·6	0·27	0·68
3 h	9·9	25·4	26·2	38·5	0·34	—
Equilibrium	9·2	51·6	24·0	15·2	1·07	1·07

FIG. 5

Time course of the methanol conversion to individual hydrocarbons, determined over the individual zeolite samples, on the total aluminium content $(Al)_t$ ○ 15 min, ● 1 h, ◑ 2 h

such active centres start only to be formed in the course of the reaction. After 2 h on stream, when a sufficient amount of those centres has been formed, the activity starts to decrease more quickly so that the final activity of the sample H-Y (after 4 h on stream) is lower than that of dealuminated samples.

Isomerization of C_4 Hydrocarbons

In the products the amounts of the individual isomers of the C_4 fraction were analytically determined. In the case of butane, the ratio i-C_4/n-C_4 was 8 to 10 with the samples H-Y, E, D, and C, and about 12 with the sample B, independent on the time on stream. The ratio of the theoretical values corresponding to the isomer mixture in equilibrium is 0·74. Also with butenes isomers the values obtained differed greatly from the equilibrium composition[8]. The relative amounts of the individual isomers determined with the sample E are given in Table II, together with the ratio i/n. (The values obtained with other zeolite samples are similar.) At the beginning of the reaction ($t = 15$ min), cis-2-butene is practically the only butene product in the gas phase. With increasing reaction time and progressing deactivation of the zeolite, the relative amount of the other isomers increases and nears the equilibrium composition. In the course of 2 h on stream the relative amount of isobutene in the gas phase increases by nearly one order of magnitude.

The ratio i/n for the total fraction $\sum C_4$, also given in Table II, is near to the theoretical value. This fact proves that butanes are formed by the subsequent hydrogen transfer to butenes. The rate of this reaction decreases with the progress of the zeolite deactivation (the methane formation rate increasing simultaneously) and the relative content of butenes in the gas phase increases. From this fact it follows that the isomeric composition of butenes, formed over zeolites by the transformation of methanol and possibly by the dimerization of ethylene, is in all cases near to the equilibrium composition, the latter being disturbed only by the subsequent hydrogen transfer reaction.

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