CONVERSION OF ALKYLAROMATIC HYDROCARBONS OVER A NICKEL–ZEOLITE CATALYST

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The conversion of polymethylbenzenes (xylenes and 1,3,4-trimethylbenzene) and some mono-alkylbenzenes (ethylbenzene and isopropylbenzene) has been studied over a metal–zeolite catalyst prepared on the basis of zeolite Y containing calcium ions and nickel. Disproportionation of the alkylaromatic hydrocarbons over the catalyst was found to be one of the main reactions. Two factors are dominant in this reaction: the acid nature of the catalyst and the basicity of the aromatic hydrocarbons. The metal atoms have also a specific function. In all cases the conversion degree of the alkylaromatic hydrocarbons in the presence of Ni—CaY is considerably higher than that in the presence of CaY. The role of the metal in the catalyst and the reaction mechanism are discussed on the basis of the experimental data.

Some problems of reaction mechanism can be elucidated by studying the reactivity of alkyl-aromatic hydrocarbons over various catalyst. The alkylaromatic compounds are of great industrial importance and this is the reason for carrying out a great number of published investigations related to the chemistry of these compounds over acid catalysts. The basic results from these investigations are included in Germain's book[1]. Special attention should be paid to catalysts containing a transition metal on a carrier. Depending on the nature of the metal atom and of the carrier the reactions of alkylaromatic compounds (alkylbenzenes) are found to undergo considerable changes in character. The catalysts Ni—Al_2O_3, prepared by coprecipitation of the corresponding nitrate salts have been extensively studied recently. In the presence of hydrogen the alkylaromatic hydrocarbons are hydrogenolytically dealkylated over such a catalyst[2-7], the basic reaction being the rupture of the terminal bond in the alkyl chain. During the past few years interesting results have been obtained which throw light on the reactions of alkylaromatic hydrocarbons taking place on zeolite catalysts in their cationic form[8-11]. These results were interpreted in terms of ionic mechanism.

In a preceding paper we have reported the high activity for the disproportionation of toluene of a catalyst prepared from a zeolite Y and containing calcium ions and nickel.[12] This results have raised the problem about the nature of the proceeding reaction(s) and the role of the nickel atoms. Extensive studies have been carried out to elucidate these basic problems. In this paper we report the results concerning the conversion of polymethylbenzenes (xylenes and 1,2,4-trimethylbenzene) and some monoalkylbenzene derivatives (ethylbenzene and isopropylbenzene) over zeolite Y containing nickel atoms.

EXPERIMENTAL

The initial substances used in this investigation (ethylbenzene, isopropylbenzene, *o*-, *m*-, *p*-xylene and 1,3,4-trimethylbenzene) were commercial products of reagent grade quality. Before use these hydrocarbons were distilled and dried over a molecular sieve 4A. The reagents used were chromatographically found to be free of impurities. The gases used — industrial electrolytic hydrogen and ultrapure nitrogen — were additionally purified from traces of oxygen over a Pd catalyst and dried then over a molecular sieve 4A.

The catalyst was prepared from a type Y zeolite (produced in USSR) of the ratio $SiO_2 : Al_2O_3 = 4.8$. The preparation of the catalyst involved consecutive ion-exchange with solution of $CaCl_2$ and $Ni(NO_3)_2$, the final product being $(Ni_{0.18}Ca_{0.72}Na_{0.1})AlO_{4/2}SiO_{4/2}.m\ H_2O$. To elucidate the role of nickel in the catalyst (Ni—CaY),* this catalyst was compared with its calcium form (CaY),* obtained by ion-exchange as an intermediate product. The catalytic experiments were carried out on a laboratory installation of a flow type at atmospheric pressure using a catalyst pelleted and then crushed in advance to 20—70 mesh grains. Before being studied the catalyst has been treated for 2 hours in a hydrogen flow at 450°C thus completing the reduction of nickel atoms. The experiments were carried out at a space velocity of $1.1\ gh^{-1}\ g_{cat}^{-1}$ and a molar ratio of hydrogen/hydrocarbon 10. A detailed description of the employed procedure is given elsewhere[12]. The experiments were performed within a wide temperature range (200 to 450 C), the lower and higher limits of this range being determined by the reactivity of the alkylbenzene used. A change of activity for a given type of catalyst was observed as function of the operational time. The data on the degree of conversion given in this paper refer to a period of time, during which the catalyst showed a constant activity, this period usually being not less than 3—4 hours.

The liquid products from the conversion of ethylbenzene and *o*-, *m*-, and *p*-xylenes were analysed using gas chromatography and a liquid phase consisting of a mixture of Bentone and lanoline (1 : 1) over Chromosorb W at 85°C. The liquid products from the reactions of isopropylbenzene and 1,2,4-trimethylbenzene were analyzed over a liquid phase of polyethyleneglycol adipate (10%) on Sterchamol at 140°C. The analysis of the gas phase obtained from the isopropylbenzene conversion was made over an isoquinoline phase at 32°C.

RESULTS

o-*Xylene.* The reactivity of *o*-xylene over the studied catalyst was investigated within the temperature range from 250 to 450°C. Three types of reactions can take place under these conditions: isomerization, disproportionation and dealkylation. The experimental data are presented in Fig. 1*a*. The principal reaction at low temperatures is the isomerization into *m*- and *p*-xylenes, the amount of *m*-xylene always exceeding that of *p*-xylene. The relative part of the disproportionation to trimethylbenzene in the overall reaction is also increased with temperature. The formation of small amounts (less than 1%) of tetramethylbenzenes at higher temperatures was also observed. Dealkylation was detected mainly at temperatures higher than 400°C.

m-*Xylene.* The conversion of *m*-xylene was studied under conditions similar to those used for *o*-xylene. The results are given in Fig. 1*b*. *m*-Xylene is subject to the same transformations as *o*-xylene; the interrelation between the separate parallel reactions of isomerization and disproportionation is different, however.

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*   These symbols are further used to denote specimen of catalysts.

p-*Xylene*. The conversion of *p*-xylene occurs under the same conditions as those for *o*- and *m*-xylenes. The results are summarized in Fig. 1*c*. From the data it is readily seen that *p*-xylene shows the highest relative reactivity. Isomerization and disproportionation of *p*-xylene are observed even at 250°C, and the equilibrium state is almost attained at 350°C. An increase of the amount of the dealkylation products, as in the case of the other isomers, was found when the temperature was increased.
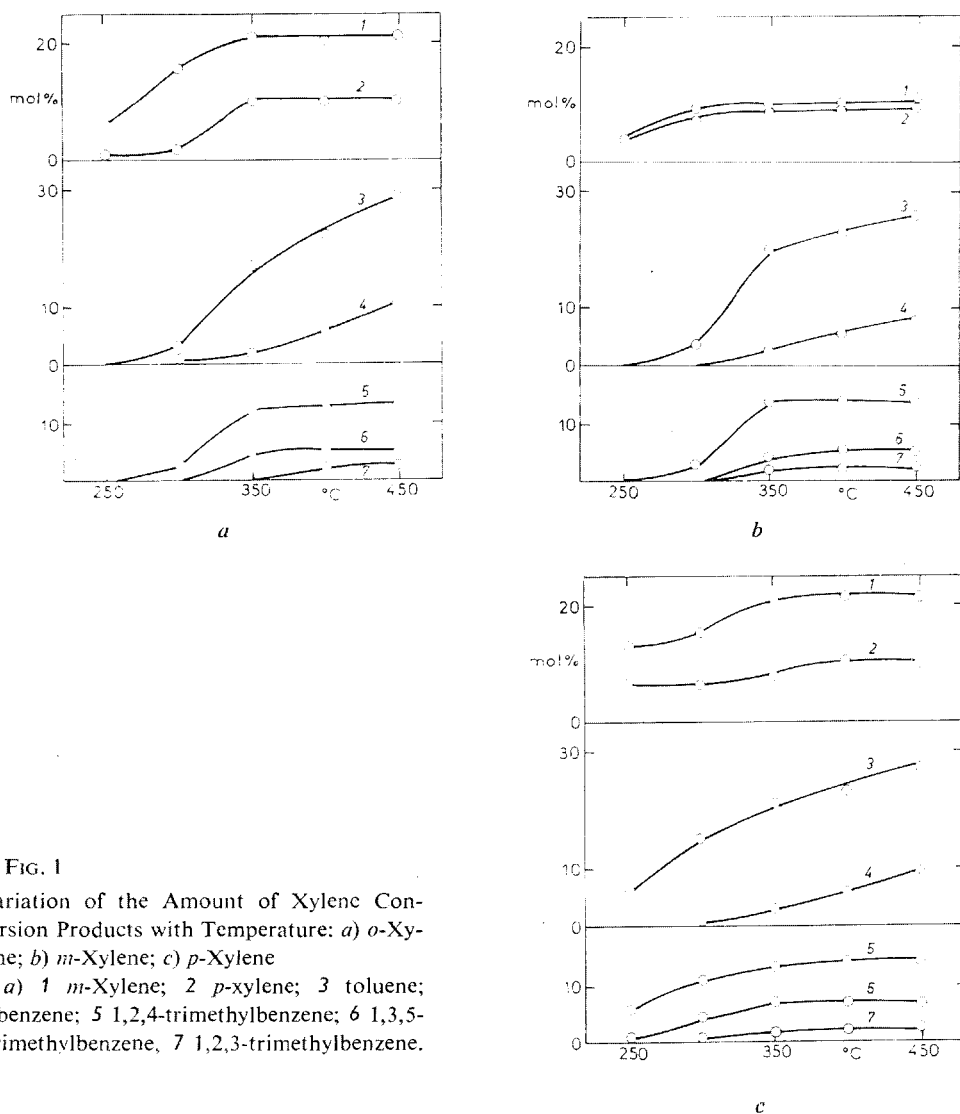

FIG. 1

Variation of the Amount of Xylene Conversion Products with Temperature: *a*) *o*-Xylene; *b*) *m*-Xylene; *c*) *p*-Xylene

a) *1* *m*-Xylene; *2* *p*-xylene; *3* toluene; *4* benzene; *5* 1,2,4-trimethylbenzene; *6* 1,3,5-trimethylbenzene, *7* 1,2,3-trimethylbenzene.

The reactivity of all xylenes was also checked over a catalyst free of nickel (CaY). As seen from Table I, the absence of nickel considerably lowers the activity of the catalyst.

1,2,4-Trimethylbenzene (pseudocumene). As seen from Fig. 2 the degree of conversion of pseudocumene even at 200°C is as large as 16·4%. If the temperature is increased up to 350°C an increase in the conversion depth up to 68·3% is observed.
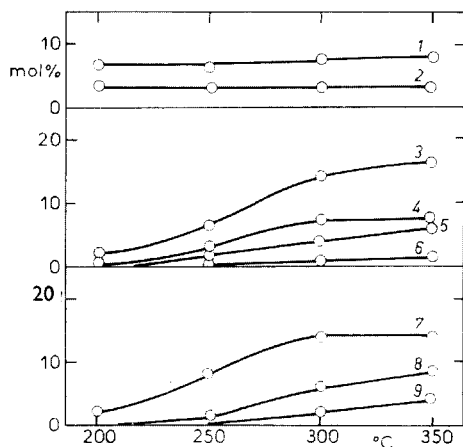

FIG. 2

Variation of the Amounts of Pseudocumene Conversion Products with Temperature

1 1,3,5-Trimethylbenzene; *2* 1,2,3-trimethylbenzene; *3* *m*-, *p*-Xylene; *4* *o*-Xylene; *5* toluene; *6* benzene; *7* 1,2,3,5-tetramethylbenzene; *8* 1,2,4,5-tetramethylbenzene; *9* 1,2,3,4-tetramethylbenzene.

TABLE I

Comparison of Activity of Ni–CaY and CaY Catalysts

Initial hydrocarbon	Catalyst	Total conversion (mol%)		Reaction products			
				isomerization		disproportionation	
		350°C	450°C	350°C	450°C	350°C	450°C
o-Xylene	Ni–CaY	65·5	90·5	31·0	31·3	32·4	40·4
	CaY	15·3	43·9	15·3	28·6	—	14·0
m-Xylene	Ni–CaY	60·8	74·8	18·7	21·20	38·8	41·4
	CaY	22·9	30·3	14·9	19·1	9·0	11·2
p-Xylene	Ni–CaY	73·1	90·2	29·1	31·2	41·6	45·4
	CaY	35·0	48·0	15·0	18·0	20·0	30·0
1,2,4-Trimethyl-benzene	Ni–CaY	68·3	—	11·1	—	52·4	—
	CaY	46·9	—	9·0	—	35·2	—
Ethylbenzene	Ni–CaY	61·9	—	—	—	36·2	—
	CaY	5·9	27·6	—	—	4·4	24·6

The temperature variation has little effect on the isomerization and dealkylation products. The increase in the total degree of conversion is due mainly to the increased amount of the disproportionation products among which the predominant component is 1,2,3,5-tetramethylbenzen. It is worth mentioning that a more prolonged period of stable operation of the catalyst is characteristic for this reaction: for more than 10 h the activity of the catalyst has not been substantially changed. If a CaY zeolite is used the reaction is found to proceed in the same manner (Table I): the degree of conversion, however, is lower.

Ethylbenzene. This conversion was studied within a temperature range of 250 to 400°C. The reaction was found to proceed at a temperature as low as 250°C, the products being only benzene and diethylbenzenes (Fig. 3). The degree of conversion increases with temperature, the process, however, is complicated by side reactions such as hydrocracking and isomerization which result in the formation of toluene, xylenes, gaseous and coke-like products. The high degree of conversion at higher temperatures is due to the intensive hydrogenolytic reaction as evidenced by the great amounts of benzene and toluene. At 300°C the catalyst is found to be operating in a stable regime for 6 hours, whereas at 400°C the period of constant activity is shorter. The substitution of nitrogen for hydrogen in the catalytic process has little effect on the total degree of conversion and on the reaction product com-
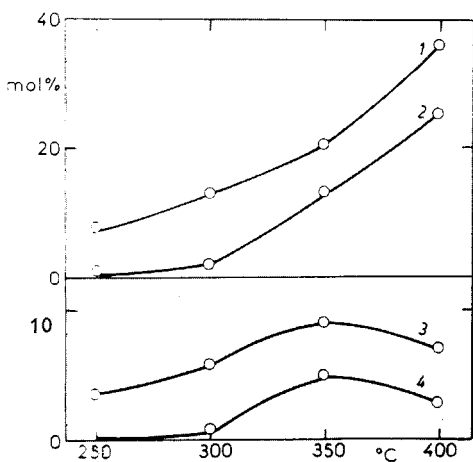

FIG. 3

Variation of the Amounts of Ethylbenzene Conversion Products with Temperature

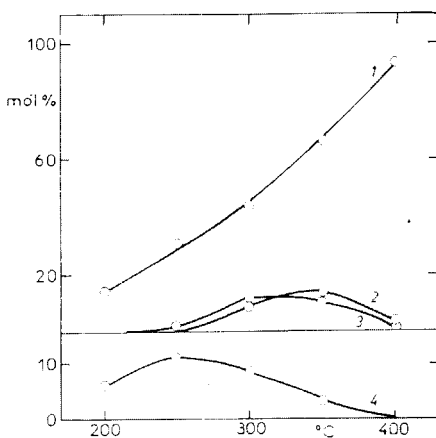 *1* Benzene; *2* toluene; *3* diethylbenzenes; *4* xylenes.

FIG. 4

Variation of the Amounts of Cumene Conversion Products with Temperature

  1 Benzene; *2* toluene; *3* ethylbenzene; *4* diisopropylbenzenes.

Table II

Calculated[13] and Experimental Data for the Equilibrium Concentrations of Methylbenzenes (mol.%)

The first row for each methylbenzene gives the calculated values.

Methyl-benzene	T, K	Benzene	Toluene	o-Xylene	m-Xylene	p-Xylene
Toluene	700	31·9	41·1	5·3	12·0	5·4
	703	22·0	64·0	3·4	6·8	3·8
	743	34·4	48·2	4·0	7·4	4·6
m-Xylene	700	6·0	24·1	9·7	21·8	9·8
	623	2·6	20·1	9·1	39·2	9·6
	673	5·9	23·1	9·8	29·5	10·1
	723	7·7	25·8	10·2	25·2	11·0
Pseudo-cumene	600	0·4	5·2	5·5	13·6	6·0
	523	0·5	1·7	3·1	3·5	3·1
	573	0·6	3·8	7·3	8·3	5·9
	623	1·5	6·7	6·7	9·7	6·4

position. In this case, however, the activity of the catalyst is changed very quickly and the catalyst is soon desactivated. In the absence of nickel the catalyst CaY is of a considerably lower activity (Table I). Moreover, the main reaction path was the disproportionation to diethylbenzenes, this finding being in agreement with the available literature data for such catalysts[9].

Isopropylbenzene (*cumene*) shows a high reactivity over the catalyst Ni–CaY. As seen from Fig. 4 the degree of conversion at temperatures as low as 200°C is 20·5%. The main reaction path of isopropylbenzene conversion is its dealkylation. The disproportionation proceeds to a considerably lower extent. The presence of ethylbenzene and toluene in the reaction products obtained over a Ni–CaY catalyst shows that for this catalyst a partial hydrogenolysis of isopropylbenzene takes place. The calcium form of the zeolite (CaY) also exhibits a considerable activity with respect to isopropylbenzene dealkylation and disproportionation. The depth of conversion of these reactions is temperature dependent. At equal conversion degrees, the amounts of toluene and ethylbenzene in the reaction product are less than in the products obtained over a Ni–CaY catalyst. The data refer to the first two working hours, with the exception of the data at 400°C; at this temperature the activity was reduced right after the first hour.

TABLE II

(*Continued*)

1,2,3-Trimethyl-benzene	1,2,4-Trimethyl-benzene	1,3,5-Trimethyl-benzene	1,2,3,4-Tetra-methylbenzene	1,2,3,5-Tetra-methylbenzene	1,2,4,5-Tetra-methylbenzene
0·4	2·6	0·9	—	0·4	—
—	—	—	—	—	—
0·1	1·0	0·3	—	—	—
2·1	14·7	4·9	1·2	3·3	2·1
1·7	13·6	4·1	—	—	—
2·0	14·1	5·3	—	—	—
1·9	13·8	5·0	—	—	—
2·9	25·5	9·2	4·3	14·3	9·7
2·9	67·8	6·4	—	8·2	0·8
3·1	41·3	7·6	2·1	13·9	6·1
3·2	31·7	7·9	4·2	13·7	8·3

DISCUSSION

The results obtained provide the evidence that the catalyst Ni–CaY is of a con-
siderable activity with respect to polymethylbenzenes and monoalkylbenzenes.
Under the conditions studied in this paper the following main reactions have been
found to take place: isomerization, disproportionation of the alkyl groups hydro-
cracking and dealkylation. The relative contributions of these reactions to the overall
reaction over the catalyst depend on the nature of the alkyl group and its position
in the benzene ring.

The isomerization of xylenes leads to the composition of the reaction product
which is controlled by thermodynamic factors. At low temperatures (under 300°C)
o-xylene and *p*-xylene conversions have been observed, the *m*-isomer being the main
reaction product of this conversion. An increase in the amount of the isomeric pro-
ducts in the reaction mixture was observed up to 350°C, this amount becoming con-
stant after 350°C and remaining such up to 450°C. The lower reactivity of *m*-xylene
and the firm trend to obtaining the *m*-isomer from *o*- and *p*-xylenes is in agreement
with thermodynamic data. It should be noted that products corresponding to the
equilibrium composition (Table II) were obtained for the three xylene isomers
at reaction temperatures higher than 350°C. This indicates that the isomerization
of xylene is a rapid reaction which at the space velocity we have used attains the

equilibrium state. These conclusions refer also to 1,2,4-trimethylbenzene, the equilibrium between its isomers being attained in practice even at $200-250°C$.

If the results obtained by the isomerization over Ni—CaY are compared with those for CaY (Table I) we see that at 350°C the activity of the latter is considerably lower. The activity with respect to isomerization for both catalysts becomes equal only at 450°C. This effect was observed for the 1,2,4-trimethylbenzene isomerization at temperatures lower than 300°C.

The disproportionation reaction is one of the main reactions taking place over the studied catalysts. The disproportionation of the methyl group of toluene[12] begins at temperatures higher than 400°C and at 470°C the conversion degree reaches the value of 35%. If the number of methyl groups is increased (as in xylenes and 1,2,4--trimethylbenzene) this is found to facilitate the disproportionation reaction, the effect being manifested mainly in lowering of the temperature at which the reaction begins. Thus for xylenes the reaction begins at 300°C, and for 1,2,4-trimethylbenzene at 200°C. It should be noted that CaY, which is inactive with respect to toluene at 400°C is of a considerable activity with respect to 1,2,4-trimethylbenzene.

The disproportionation of the ethyl group in ethylbenzene to diethylbenzene and benzene occurs to a much greater extent even at 250°C and the disproportionation of cumene is observed at even lower temperatures (at approx. 200°C). When the reaction of these hydrocarbons was carried out at higher temperatures the amount of the disproportionation reaction products was found to decrease. Thus from ethylbenzene at temperatures higher than 350°C the relative content of diethylbenzene in the reaction product is considerably lower than in that at 300°C. This effect could be observed for cumene even at 250°C. Obviously other reactions, in particular that of hydrocracking of the alkyl chain, interfere with the disproportionation reaction. It should be noted that it is extremely difficult to make an exact assessment of the quantitative ratios between the disproportionation and hydrocracking reactions on the basis of the reaction product composition.

If the obtained experimental data are compared with the calculated equilibrium constants it is readily seen (Table II) that within a specific temperature range, the experimental and calculated values are in good agreement. This agreement provides the basis for claiming that hydrocracking is rather slow in this temperature range.

The presence of a metal and a carrier with expressed acidic functions raises the question about the role of the metal in the catalyst and about the reaction mechanism. The experimental data on cumene conversion over Ni–CaY (Fig. 4) show that at 200°C dealkylation and disproportionation of the isopropyl group are the only reactions that take place. At 400°C the main product is benzene, the conversion being 97%. The presence of small amounts of toluene (3·2%) and ethylbenzene (0·6%) indicates that, parallel to hydrocracking, hydrogenolysis (rupture of methyl groups) occurs to a slight extent. The high activity of the catalyst is indicative of the presence of strong acidic sites which determine the course of the reactions of ionic type.

The basicity of these compounds is of particular interest for the elucidation of the reactivity of the alkylaromatic hydrocarbons with respect to the disproportionation reaction. The equilibrium constants for the formation of a carbonion in the system alkylbenzene–HF are a function of the basicity of the aromatic compound[14] and this function increases parallel to the increase in number of the alkyl substituents as follows: Benzene $K = 3{\cdot}3 \, . \, 10^{-8}$, toluene $K = 2{\cdot}2 \, . \, 10^{-7}$, *o*-xylene $K = 4{\cdot}2 \, . \, 10^{-7}$, 1,2,4-tri-methylbenzene $K = 4{\cdot}5 \, . \, 10^{-3}$. These data are in good agreement with the experimental data presented above. Comparing the temperatures at which an equal conversion degree with respect to disproportionation is obtained a similar series of increasing reactivity is formed: $C_6H_5CH_3 < C_6H_4(CH_3)_2 < 1,3,4\text{-}C_6H_3(CH_3)_3$.

The observed differences in the activity of the catalysts CaY and Ni—CaY may be interpreted in terms of the basicity difference of the studied compounds. Thus CaY is active mainly with respect to strongly basic compounds (1,3,4-trimethylbenzene and cumene). The incorporation of nickel atoms produces and active catalyst with respect to compounds of a weaker basic character (toluene and xylenes). This finding is an indirect indication that nickel atoms favour the increase of the acid functions of the catalyst. It may be assumed that after the reduction of Ni^{2+} to Ni^0 strongly acidic sites are formed in the zeolite structure. Concurrently with the formation of acidic sites, the metallic nickel may favour the activation of the initial hydro-carbons thus facilitating their further conversion. It should be noted, however, that in order to prove the reaction mechanism, more data are needed. The metal in the catalyst Ni–CaY plays an additional role besides: in the presence of hydrogen it helps the hydrogenation of some of the intermediate compounds which might block irreversibly the active sites of the catalyst.

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