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Coking, Aging, and Regeneration of Zeolites

XIII. Composition of the Carbonaceous Compounds Responsible for the Deactivation of a USHY Zeolite during Toluene Disproportionation

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The rate of formation and the composition of the carbonaceous compounds (coke) responsible for the deactivation of an ultrastable HY zeolite during toluene transformation were determined from 120 to 450°C. At low reaction temperature these compounds, consisting mainly of toluene trimers, methylanthracenes, and phenanthrenes, are the only reaction products. Being less bulky, they are retained in the zeolite pores because of their low volatility and because of their strong adsorption. At high temperature, the disproportionation of toluene is the main reaction and the coke molecules are sterically blocked in the zeolite. At 350°C pyrenic compounds are the main coke components. Located in the supercages, they limit, but do not block, the diffusion of reactant to the acid sites and that of products from the acid sites to the outer surface of the crystallites. This limitation is responsible for the activity decrease and the increase in selectivity for the smallest disproportionation products. At 450°C the coke molecules are bulkier and highly polyaromatic and deactivation is due to a blockage of the access of the reactant to the acid sites. Mechanisms are proposed to explain the formation of the various coke components.

INTRODUCTION

Deactivation of acid zeolites is caused mainly by the retention of carbonaceous compounds ("coke") inside the pores or on the outer surface of the crystallites. A significant effort was made recently to specify the factors that govern the rate of coking, the composition, and the location of coke, as well as the mode(s) of zeolite deactivation. Thanks to a combination of different techniques such as catalytic activity measurements, separation of coke from the zeolite, and analysis by GC, ^{1}H NMR, MS and other methods, adsorption on the coked zeolites the effects of the pore structure on the modes of coking and of deactivation of zeolites during cracking are now well-understood (*1*). Coking and deactivation, however, depend also on the characteristics of the active sites and on the operating conditions: reaction time, temperature (*2–12*), pressure, and nature of the reactant (*6, 13–17*). Relatively few studies concern the influence of the nature of the reactant, the reactant used being often olefinic or paraffinic, or more rarely aromatic.

Maixner *et al.* (*6*) showed that the rate of coke formation on an LaY zeolite was lower from toluene than from 1-hexene and even from 2,2,4-trimethylpentane, whatever the reaction temperature (from 100 to 350°C). The coke deposits were characterized by elemental analysis and CP/MAS ^{13}C NMR spectroscopy. The compounds remaining on LaY after exposure to toluene at 100°C consist of the unconverted feed while at 350°C they consist of polynuclear aromatics. During cumene (*18, 19*) and ethylbenzene (*20*) transformation the formation of coke and the deactivation, which are very

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slow when aromatics transform through disproportionation, become rapid when aromatics undergo dealkylation. Coke formation occurs from the olefins produced by dealkylation and not directly from the aromatic reactant (*18*). However, as on silica–alumina (*21*), the rate of coking on zeolites increases very much with the basicity of the aromatic reactants and becomes close to and even greater than that of olefinic reactants (*22*). As from toluene on LaY, the carbonaceous deposits responsible for the deactivation of various protonic zeolites during 1-methylnaphthalene conversion consist of unconverted reactant at low temperatures and of condensed ring aromatics at high temperatures (*10*).

The aim of this work is to specify the modes of coking and of deactivation of an ultrastable HY (USHY) zeolite during toluene disproportionation at temperatures between 120 and 450°C. For this, emphasis will be placed on the determination of the coke composition. The technique developed from coke characterization consists of dissolving the zeolite in a solution of hydrofluoric acid, recovering the coke components in an organic solvent, and analyzing the soluble components by GC, ^{1}H NMR, and MS (*11*). At low temperature the only reaction products are dimers and trimers of toluene and compounds resulting from their cyclization and their dehydrogenation; they are retained in the zeolite pores because of their low volatility and their adsorption. At high temperature, disproportionation of toluene is the main reaction. Deactivation is due to highly polyaromatic molecules sterically blocked in the zeolite. Mechanisms are proposed to explain the formation of the various coke components.

EXPERIMENTAL

USHY was obtained by calcination at 500°C under a 10 h dry-air flow of an ultrastable NH_4 zeolite (LZY82 from Union Carbide). The framework Si/Al ratio deduced from the unit cell parameter by using the equation proposed by Breck and Flanigen (*23*) was equal to 4.8.

The transformation of toluene was carried out in a flow reactor at 120, 200, 350, and 450°C, with $P_{\text{toluene}} = 0.3$ bar and $P_{\text{nitrogen}} = 0.7$ bar. Reaction products were analyzed on line by GC using a 50 m polyphenylether capillary column. For the kinetic study of coking, the WWH (grams of toluene injected per gram of zeolite per hour) was equal to 32 h^{-1}. The coked samples used for coke analysis were obtained by operating with a WWH value of 3.2 h^{-1}. The experimental methods used to determine the H/C ratio of the carbonaceous deposits as well as those used to recover and to analyze the coke components have already been described (*11*).

RESULTS

1. Conversion of Toluene and Coke Formation

At 120 and 200°C there is no apparent transformation of toluene. At 350 and 450°C toluene is converted into various hydrocarbons. Figure 1 shows that the initial activity of USHY for disproportionation is about five times greater at 450°C than at 350°C. The deactivation rate is a little dependent on the temperature: at both these temperatures

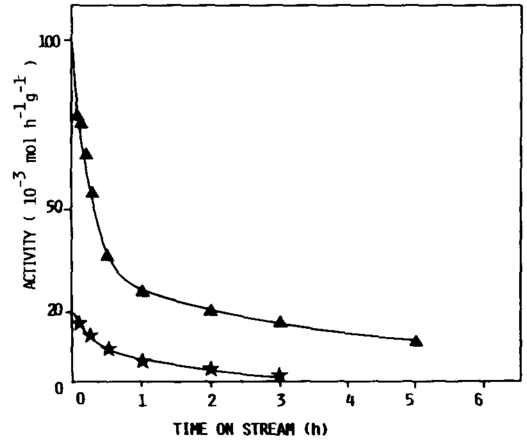


FIG. 1. Disproportionation of toluene on USHY at 350°C (★) and 450°C (▲). Activity $A(10^{-3}$ mol h^{-1} $g^{-1})$ as function of time-on-stream t (h).

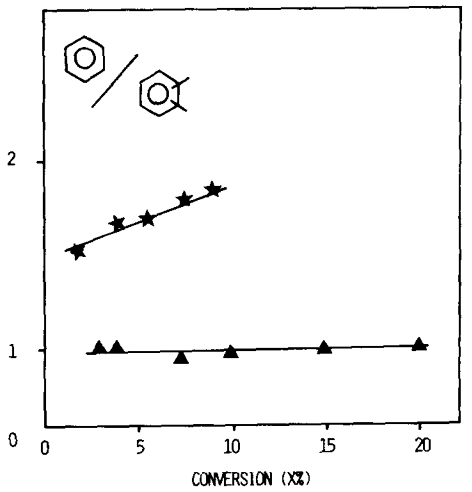


FIG. 2. Disproportionation of toluene on USHY at 350°C (★) and 450°C (▲). Molar benzene/xylenes ratio as function of the conversion of toluene (*X*%).

the activity after 1 h of reaction is equal to about 30% of the initial activity. Benzene and xylenes are the main products (over 90 wt%). C_2–C_4 hydrocarbons, ethylbenzene, and trimethylbenzenes can also be observed. At 450°C, the benzene/xylenes molar ratio is close to 1, which is the value expected from a simple disproportionation of toluene. At 350°C this ratio is greater than 1 (Fig. 2). The distribution of xylenes depends on the reaction temperature and on the time-on-stream *t* (hence on the deactivation). At 450°C this distribution is close to that found at thermodynamic equilibrium (50% *meta*, 25%, *ortho*, 25% *para*) for low *t* values. For high *t* values the *para* isomer is little favored (about 30%). At 350°C the *para* isomer is always favored: 30% for low *t* values to 40% for high *t* values (Fig. 3).

Whatever the reaction temperature there is a retention of heavy compounds ("coke") in the zeolite. This formation of coke is responsible for the deactivation of the zeolite observed at 350 and 450°C. The rate of coke formation increases with the temperature rising after 1 h of reaction from 2.3 wt% at 120°C to 9.2 wt% at 450°C (Fig. 4).

2. *Coke Composition*

To specify the composition of coke, 1 g of zeolite was used instead of 0.1 g in the kinetic study of coking, the other operating conditions being maintained. The color of the coked samples depends on the reaction temperature. After 6 h of reaction the zeolite

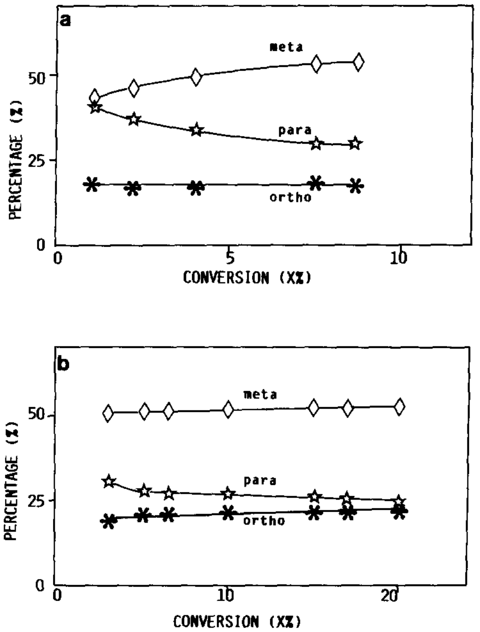


FIG. 3. Disproportionation of toluene on USHY at 350°C (a) and 450°C (b). Distribution of xylenes as function of the conversion of toluene (*X*%).

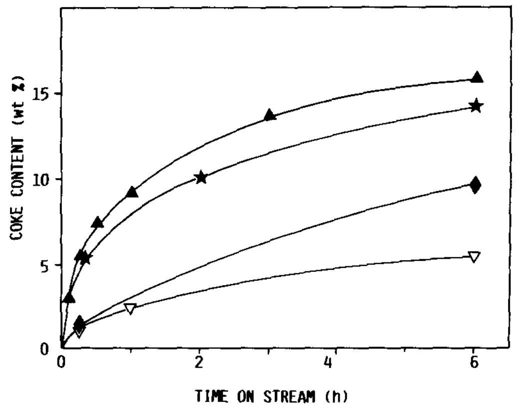


FIG. 4. Coke content of the catalyst (wt%) against time-on-stream *t* (h). 120°C (▽), 200°C (◆), 350°C (★), 450°C (▲).

TABLE 1

Characteristics of the Coked Samples

T(°C)	t (h)	wt% C	H/C	Soluble coke (wt%)
120	6	0.9		100
200	6	1.6	1.1	100
350	6	8.2	0.8	100
450	0.25	3	0.75	55
	6	14	0.5	10

Note. t, time-on-stream; wt% C, percentage of coke; H/C, atomic hydrogen to carbon ratio.

was beige at 120°C, yellow at 200°C, brown at 350°C, and black at 450°C. The coke content of the samples is given in Table 1: after 6 h it rises from 0.9 wt% at 120°C to about 14 wt% at 450°C.

2.1. H/C ratio and yield of dissolution in methylene chloride. The atomic H/C ratio decreases (i.e., the aromaticity increases) when the reaction temperature increases (Table 1). However, the experiments carried out at 450°C for different reaction times show that this H/C decrease is due partly to the increase in the reaction temperature and partly to the increase in time-on-stream (hence in the coke content).

After dissolution of the zeolite in a hydrofluoric acid solution all the components of the coke deposited at 120, 200, and 350°C can be dissolved in CH_2Cl_2. At 450°C the yield of dissolution for the coke content of 3 wt% is equal to 55% and for 14 to 10%. The nonsoluble part remains as small black particles. They are probably constituted of highly condensed polyaromatic compounds.

2.2. Analysis of the soluble coke by GC, ^1H NMR, and MS. GC analysis shows that the soluble cokes are always very complex mixtures. The lower the temperature the more complex the mixture (Fig. 5).

^{1}H NMR shows that the aromaticity of the coke increases with the reaction temperature. The percentage of aromatic protons (H_{AR}, 7 ppm $< \delta <$ 9 ppm) increases greatly: after 6 h of reaction at 120°C, 25% of the protons are aromatic while at 450°C about 75% are aromatic. Moreover, while at 120°C, the ratio of the percentages of alkylaromatic (H_{AA}, 2 ppm $< \delta <$ 2.5 ppm) to aromatic protons (H_{AR}) is high (about 3); at 450°C it is very low (about 0.15). These changes are due not only to a direct effect of the reaction temperature on the coke composition but also to an effect of the time-on-stream and hence of the coke content (see in Fig. 6 the values of H_{AR} and of H_{AA}/H_{AR} obtained for time-on-stream of 0.25 and 6 h at 450°C).

The MS analysis of the soluble coke was carried out at low ionization energy (10 eV) so as to avoid fragmentations. The coke components can be classified into families with C_nH_{2n-z} as the general formula; i.e., the constituents of a family have molecular weights differing by 14 units, which can correspond to the substitution of a methyl

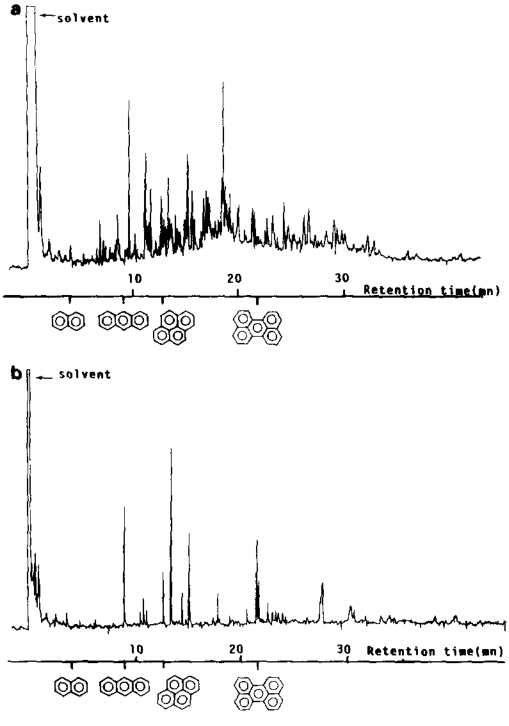


FIG. 5. Gas-phase chromatographs of soluble coke (a) 200°C, (b) 350°C. Various aromatic compounds are indicated as references.

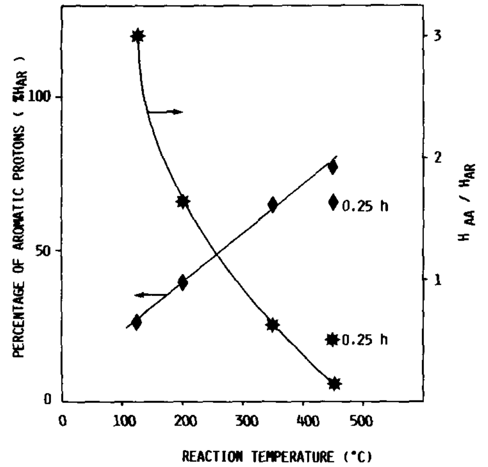


FIG. 6. Analysis of the soluble coke by ^1H NMR spectroscopy. Change in the percentages of aromatic proton (H_{AR}) and in the alkylaromatic/aromatic protons (H_{AA}/H_{AR}) as function of reaction temperature (T, °C). The figures marked 0.25 h correspond to the values obtained for a shorter time-on-stream (0.25 h instead of 6 h).

group for a hydrogen. The general formula of the main families, the number of unsaturations + cycles (In + Cy), the molecular weight M, and the number of carbon atoms (n_C) of the family constituents are given in Table 2. The number of unsaturations + cycles is deduced from the general formula: In + Cy = $z/2 + 1$. It can be seen that In + Cy (i.e., the aromaticity) increases with the reaction temperature. A good agreement is found between the experimental value of H/C and the average value deduced from the formula of the soluble coke components at 200 and at 350°C.

An estimation of the distribution of the soluble coke constituents was made from the heights of the mass spectrometry peaks (Table 2). At 120°C, the main constituents of the soluble coke belong to the C_nH_{2n-18} family (c) and to the C_nH_{2n-22} family (d). There are only small amounts of C_nH_{2n-14} (a) and of C_nH_{2n-16} (b) compounds. At 200°C, there are three main families (about 30% of each): C_nH_{2n-18} (c), C_nH_{2n-22} (d), and C_nH_{2n-28} (e). At 350°C the C_nH_{2n-22} (d) and C_nH_{2n-28} (e) families become preponderant while at 450°C for both coke contents (3 and 14%) it is the C_nH_{2n-26} (g) and C_nH_{2n-32} (f) families that are preponderant.

TABLE 2

Main Components of the Coke Soluble in Methylene Chloride

T	Coke (wt%)	Main families	In + Cy	Molecular weight M	n_c
120°C	0.9	a C_nH_{2n-14}	8	154–196	12–15
		b C_nH_{2n-16}	9	166–236	13–18
		c C_nH_{2n-18}	10	192–262	15–20
		d C_nH_{2n-22}	12	244–300	19–23
200°C	1.6	b C_nH_{2n-16}	9	166–236	13–18
		c C_nH_{2n-18}	10	178–220	14–17
		d C_nH_{2n-22}	12	202–272	16–21
		e C_nH_{2n-28}	15	252–322	20–25
350°C	8.2	c C_nH_{2n-18}	10	178,192	14,15
		d C_nH_{2n-22}	12	202–230	16–18
		e C_nH_{2n-28}	15	252–322	20–25
		f C_nH_{2n-32}	17	276–332	22–26
450°C	3	d C_nH_{2n-22}	12	202–230	16–18
	and	f C_nH_{2n-32}	17	276–346	22–27
	14	g C_nH_{2n-26}	14	254,268	20,21
		h C_nH_{2n-36}	19	328,342	26,27

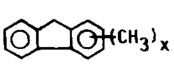
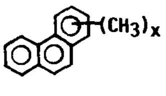
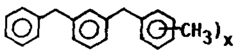
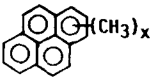
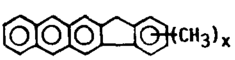
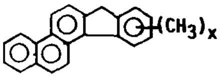
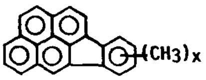
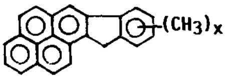
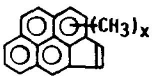
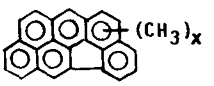
Note. In + Cy, Number of unsaturations + cycles; n_C, number of carbon atoms.

3. *Identification of the Soluble Coke Components by GC–MS*

The components of the soluble coke were identified by GC–MS coupling. The probable formula of the main constituents is given in Table 3 with their boiling points and their sizes. It must be noted that the compounds having C_nH_{2n-22} as general formula belong to two distinct families: one called d, whose constituents are formed of three molecules of benzene linked by methylene bridges, and

TABLE 3

Formula of the Main Components of the Coke Soluble in Methylene Chloride

Family	Formulae		Main components			
			T(°C)	x	bp (°C)	Size (Å)
a		x=1	120	1	290	(6x9.5)
b		x=1	120	1	295	(6x9.5)
			200	1		
c			120	3	360	(6x9.5)
or			200	1	340	(6x8.5)
		0 ≤ x ≤ 6	350	0	340	
d			120	2	> 360	(6x15.5)
		0 ≤ x ≤ 3	200	0	> 360	
d′			200	1	> 395	
			350	0	> 395	(8x8.5)
		0 ≤ x ≤ 2	450	0		
e			200	1	> 400	(6x15.5)
or		0 ≤ x ≤ 5				
			350	0	> 400	(8x14)
f			350	2	> 450	(8x14.5)
or		0 ≤ x ≤ 4				
			450	0	> 450	(8x13)
g			450	2	> 450	(8.5x9.5)
		0 ≤ x ≤ 1				
h			450	2	> 450	(8.5x13)
		0 ≤ x ≤ 3				

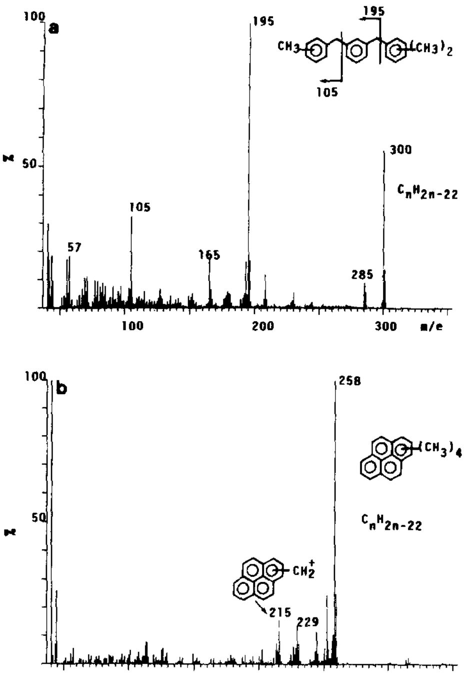


FIG. 7. Examples of identification by GC–MS coupling of the coke components.

the other called d′, whose constituents have a pyrenic skeleton. Figure 7 shows two examples of how the developed formula could be deduced from the mass of the fragments found in the MS spectrum.

DISCUSSION

Whatever the reaction temperature, heavy carbonaceous compounds (coke) remain in the Y zeolite. The cause of the retention of these compounds, the effect of coke on the rate and on the selectivity of the toluene transformation, and the mode of coke formation are examined.

1. Cause of the Retention of Coke in the Zeolite

At 120 and 200°C, various reaction products are formed but these products remain blocked in the zeolite. They are not very bulky (Table 3) and therefore their retention is not due to a steric blockage. They are retained in the zeolite because of their low volatility (their boiling point is higher than the reaction temperature (Table 3)) and also because of their chemical or physical adsorption.

At 350 and 450°C disproportionation, isomerization and cracking products are desorbed from the zeolite while heavier products (coke) remain blocked in the zeolite. At 450°C part of the coke is insoluble in methylene chloride; this insoluble coke is black and therefore probably constituted of highly polyaromatic molecules. At this temperature, it can be considered that the molecules of the soluble coke are sterically blocked in the zeolite supercages. Indeed, their size is such that these molecules can be accommodated in the supercages but can only emerge with great difficulty. This is also the case for most of the coke molecules formed at 350°C.

2. Toluene Transformation and Coke Formation

Coke is responsible for the zeolite deactivation. Figure 8 shows that at low coke content the deactivating effect of coke is practically the same at 350 and 450°C. At high coke content the deactivating effect of coke is more pronounced at 350°C than at 450°C.

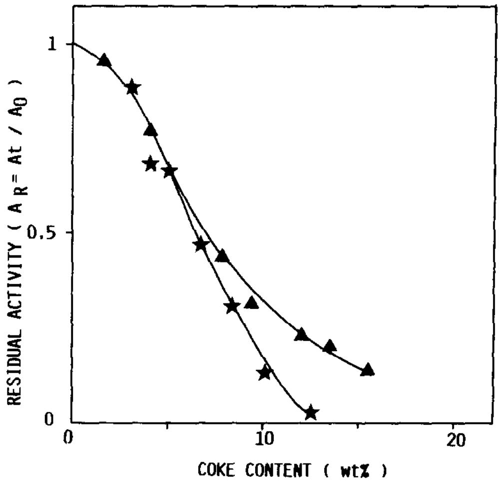


FIG. 8. Residual activity ($A_R = a_t/a_0$; a_t, activity for t and a_0, initial activity) of the zeolite USHY versus the coke content (wt%) at 350°C (★) and 450°C (▲).

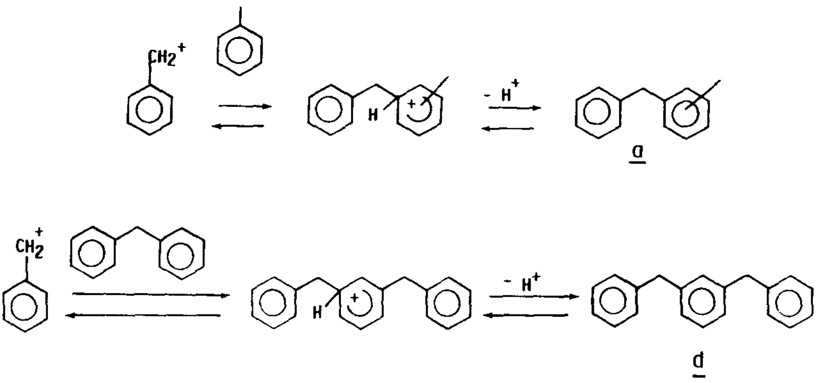
However, it must be noted that the components of coke are bulkier at 450°C than at 350°C. Therefore the number of coke molecules per gram of coke is greater at 350°C than at 450°C. This means that, at least initially, the deactivating effect of a coke molecule is smaller at 350°C than at 450°C. It is also the case at high coke contents. Indeed, 8.2 wt% coke at 350°C, which corresponds to about 2.1×10^{20} molecules of coke per gram of zeolite (number estimated according to Ref. (*24*)), causes a decrease of the activity of about 70% while 14% coke at 450°C, which corresponds to about 1.6×10^{20} molecules per gram of zeolite, causes a decrease of the activity of about 85%. The greater deactivating effect of the coke molecules at 450°C can be related to their greater size. At 350°C, a proportion of the coke molecules are much smaller than the supercages (e.g., d′, Table 3) and reactant and products can continue to diffuse through the supercages occupied by these coke molecules. This is not the case at 450°C: the soluble coke molecules are bulkier than at 350°C and block the diffusion of reactant and products through the supercages. Moreover, at 450°C the bulky molecules constituting the nonsoluble coke can either occupy several supercages or, when deposited on the outer surface, can block the access to several supercages (*1*).

Benzene and xylenes are the main reaction products at 350 and 450°C. These compounds (except *m*-xylene) result from toluene disproportionation. A large amount of *m*-xylene is found, however, which shows that the isomerization of xylenes is faster than the disproportionation of toluene. At 350°C the benzene/xylenes molar ratio is greater than 1 and the percentage of *p*-xylene (30 to 40%), the smallest isomer, is higher than its percentage at thermodynamic equilibrium (25%). This shows that at this temperature there are limitations to the desorption of the bulkiest products. This is no longer the case at 450°C: the benzene/xylenes molar ratio is close to 1 and xylenes are almost formed in their thermodynamic equilibrium mixture. At least a part of the diffusion limitations found at 350°C is due to coke deposited in the supercages. Indeed, the selectivity depends on the zeolite coke content. This change in selectivity means that the access of toluene to the acid sites and the diffusion of disproportionation products from the acid sites to the outer surface of the crystallites are not blocked but only limited. This is what was proposed above as an explanation of the less pronounced deactivating effect of the coke molecules at 350°C. A proportion of the coke molecules is smaller than the supercages (e.g., d′, Table 3) and reactant and products diffuse through the supercages in which these coke molecules are located. Obviously the diffusion is slowed down and the less bulky products (benzene, *p*-xylene) desorb preferentially. At 450°C coke decreases the activity but has practically no effect on the selectivity. Therefore the coke molecules not only limit the diffusion of reactant and products, but block it. This was expected since the molecules of coke formed at 450°C are very bulky. In particular the size of the soluble coke molecules is close to that of the supercages. We can thus conclude that the mode of deactivation depends on the reaction temperature. At low reaction temperature, deactivation is due to a limitation of the access to the acid sites and at high temperature to a blockage of this access.

The ratio of the rates of coking and of disproportionation decreases when the temperature increases: this ratio is equal to ∞ at 120 and 200°C, between 0.25 (t = 5 min) and 0.06 (t = 3 h) at 350°C and between 0.07 and 0.02 at 450°C. The high selectivity for coking found at low temperature can be related to limitations in the diffusion of reaction products. The contact time of these molecules with the acid sites is long enough to allow condensation reactions to occur. As the bulky and poorly volatile products formed diffuse very slowly, they undergo various transformations and lead to "coke."

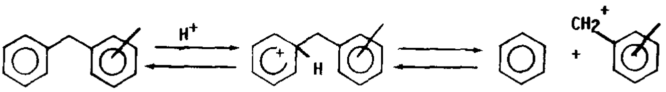
3. Mode of Coke Formation

3.1. At 120°C, coke is constituted of four families of components (*a* to *d*, Table 3), the major components being methyl anthracenes or phenanthrenes. The components of *a* and *d* families result from a nucleophilic attack of a benzylic carbocation (formed by hydride transfer from toluene to a preexisting carbocation or to a protonic site) by a molecule of toluene or of diphenyl methane.



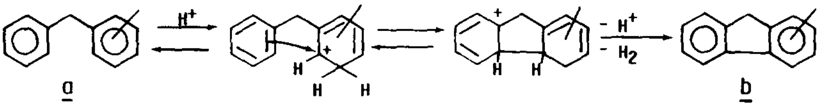
(1)

The *a* compounds are intermediates in toluene disproportionation (*25*). They lead to benzene and xylenes through the following steps:



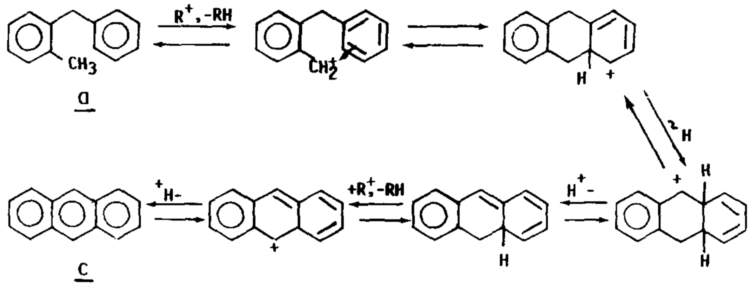
(2)

The fluorenic compounds (family *b*) result from dehydrogenation of *a* compounds. This dehydrogenation, very easy by thermal treatment, is probably catalyzed by protonic sites:



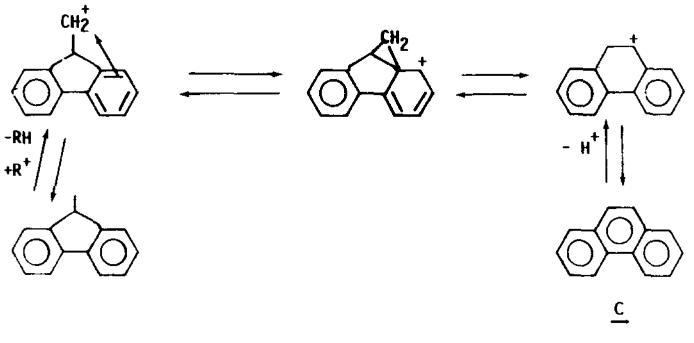
(3)

Anthracenic compounds (family *c*) could result from the following reactions:



(4)

Phenanthrenic compounds (family *c*) would be formed from methylfluorenes:



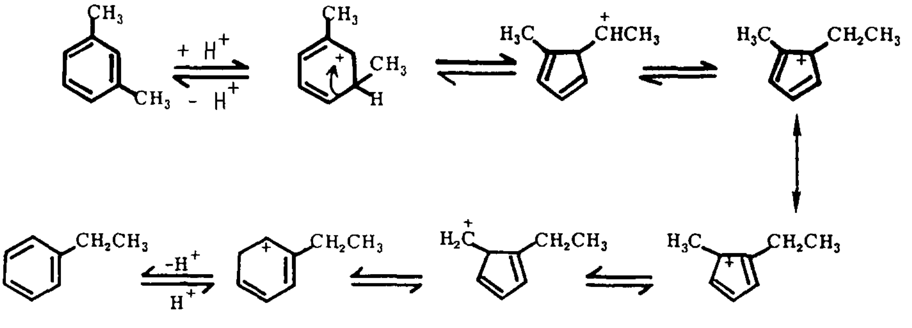
(5)

However, it can be noted that an unstable primary carbenium ion is involved in their formation.

3.2. At 200°C, coke comprises *b*, *c*, and *d* compounds already found at 120°C. Moreover, pyrenic (*d'* family) and indeno-anthracenic or phenanthrenic (*e* family) compounds appear. The formation of *d'* compounds occurs through the reactions involved in the formation of *c* compounds. The *e* compounds can be formed through the reactions involved in the formation of *a* and *b* compounds.

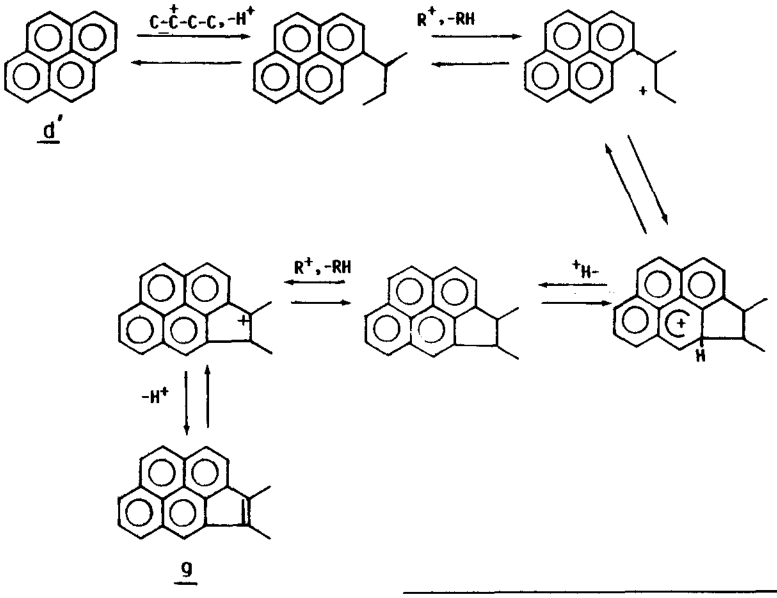
3.3. At 350°C, coke comprises *c*, *d'*, and *e* families found at 200°C. Indenopyrenic compounds (*f* family, Table 3) appear. Their formation from pyrene (*d* family) occurs through the reactions involved in the formation of *b* compounds: nucleophilic attack of a benzylic cation by a molecule of pyrene followed by dehydrogenation.

3.4. At 450°C, the soluble coke comprises four families of compounds: *d'* and *f* found at 350°C and *g* and *h*. These latter compounds cannot be formed through the reactions involved in the formation of all the other compounds. Since they exist in the coke resulting from the transformation of *n*-heptane (*1*), propene (*11*), or cyclohexene (*9*), it is probable that their formation requires olefinic compounds. Light C_2–C_4 olefins are moreover observed in the reaction products at this temperature. They are probably formed through successive isomerization of polymethylbenzenes (into ethyl or propylbenzenics) and dealkylation. The mechanism of dealkylation reactions is well known. The following mechanism was proposed by Pines (*26*) for the isomerization of xylenes into ethylbenzene:



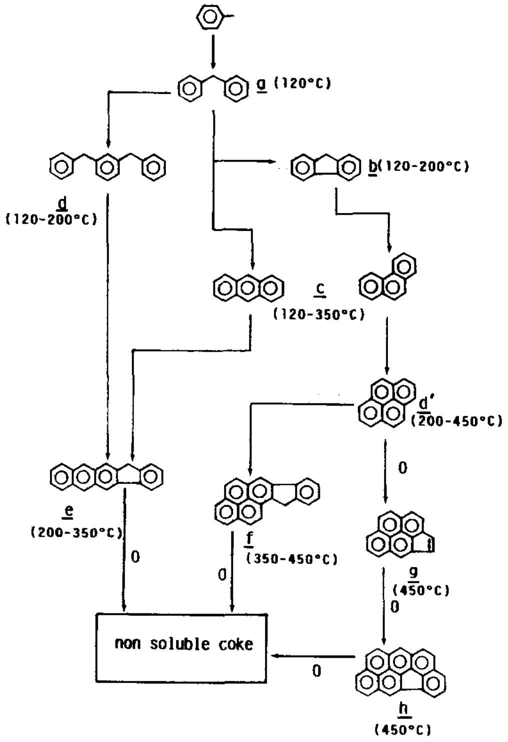
(6)

Alkylation of aromatics by olefins followed by cyclization then aromatization through hydrogen transfer reactions allow one to explain readily the formation of *g* (reaction 7) and *h* compounds as well as that of the highly polyaromatic molecules that constitute the nonsoluble coke.



(7)

Figure 9 shows how the main families of coke components are formed. This scheme is in good agreement with the change in the yields of the main coke families as a function of reaction temperature (Figs. 10a–10b) and for 450°C as function of coke content (Fig. 10c). The yields were equal to the products of the coke content by the weight percentages of the compounds of the families (estimated from the MS analysis carried out at low ionization energy). Figure 10a shows that *e* and *d'* compounds result probably from the transformation of *d* compounds. From Figs. 10a and 10b it can be concluded that *g* and *h* compounds and nonsoluble coke are formed from *e* and *d'* compounds and from Fig. 10c that nonsoluble coke results at least from the transformation of *e*, *f*, and *g* compounds.



• methyl groups are not indicated in the formulae

• O = olefins

FIG. 9. Formation of the coke components: Reaction scheme.

CONCLUSIONS

Coking and deactivation of the USHY zeolite during toluene transformation depend on the reaction temperature:

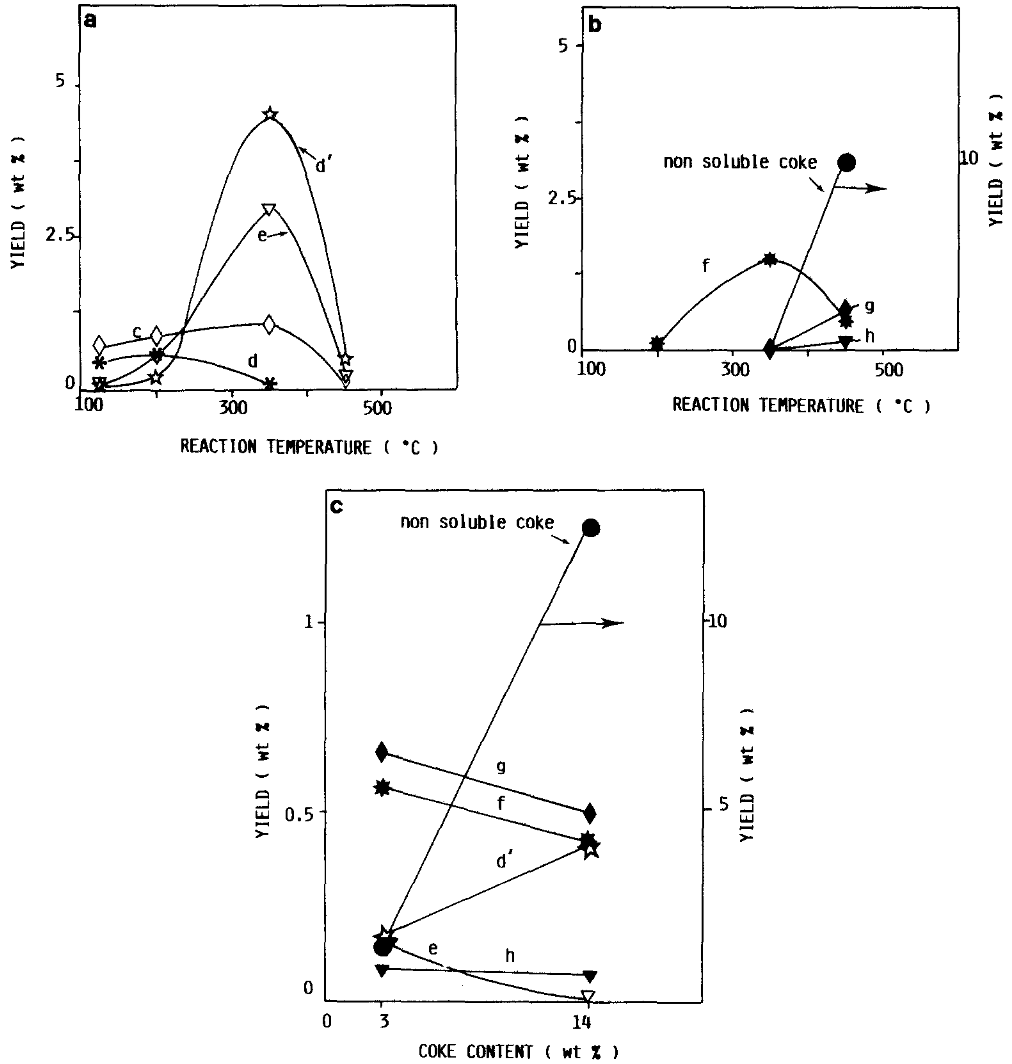


FIG. 10. Yields in the main coke components (wt%) as a function of reaction temperature T(°C) (a and b) and as function of coke content at 450°C (c).

—At low reaction temperature the only reaction products are the intermediates of toluene disproportionation and their products of cyclization and dehydrogenation blocked in the zeolite pores because of their low volatility and of their adsorption.

—At high reaction temperature the disproportionation of toluene is the main reaction. At 350°C polyaromatic compounds sterically blocked in the zeolite pores limit the diffusion of the reactant to the acid sites or that of the products from the acid sites to the outer surface of the crystallites. This limitation is responsible for a decrease in activity and an increase in the selectivity for the smallest disproportionation products: benzene and *p*-xylene. At 450°C, coke has nearly no effect on the selectivity, which means that deactivation is due to a blockage of the access of the reactant to the acid sites. This change in the mode of deactivation is due to an increase in the size of the coke molecules. Coke molecules having a size close to that of the supercages are formed initially. These molecules lead to very bulky and highly aromatic molecules, which, as was shown in the case of coke formed during *n*-heptane cracking at 450°C (*27*), probably overflow onto the outer surface of the crystallites.

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