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Characterization of the Coke Formed During *o*-Xylene Isomerization over Mordenites at Various Temperatures

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Coking over two H-mordenites (framework SiO_2/Al_2O_3 ratios of 15 and 75) was studied during *o*-xylene isomerization at temperatures between 523 and 723 K. Despite its lower acid site density the deeply dealuminated sample was the most active and more stable. This is due to the presence of mesopores created during the dealumination which render the diffusion of organic molecules quasi tridimensional, thus reducing both diffusive constraints and the deactivating effect of coke. With both samples coke aromaticity increased and the yield in coke soluble in methylene chloride decreased as the temperature increased. The composition of this coke fraction was strongly affected by reaction temperature but not by the characteristics of the mordenite samples. Whatever the temperature, coke components remained trapped in the mordenite pores. At low temperature, this trapping was due to their low volatility and/or strong adsorption, at high temperature to their steric blockage. Coke oxidation was practically independent of the coke content and composition but was favoured by the density of the acid sites.

1. INTRODUCTION

Coke formation is the main cause of catalyst deactivation in hydrocarbon reactions over acid catalysts. In the case of zeolites, coke refers to all carbon compounds formed during the reaction, polyaromatics or not, which are responsible for zeolite deactivation due to their retention both within the pores and on the outer surface of the crystallites (1).

The knowledge of coke composition is important for setting up the modes of coke formation and deactivation. Spectroscopic methods, such as "*in situ*" FT-IR, C^{13} NMR, UV-VIS, and EPR, give information on the coke content, the chemical nature of coke during and after coking, the nature of the active sites and how coke affects them, but not on the coke composition. For such, the best results are obtained from the simple methodology developed by Magnoux (2).

As has been previously shown, the rate of coke formation and coke composition both depend on the pore structure of the zeolite (1, 3–9), its acid characteristics (1, 3–6, 10), the reaction temperature (2–6, 8, 11–13), and the nature of the reactant(s) (3–6, 12–14).

Besides the kinetics of the various steps involved, both chemical equilibrium and the causes of coke retention are also strongly influenced by the temperature (6). At low temperatures, condensation reactions are thermodynamically favoured and retention is mainly due to the low volatility of the oligomers. Since these reactions are exothermic, the yield of simple condensation products at high temperatures is low. So, as temperature rises, other reactions (such as hydrogen transfer reactions) that lead to thermodynamically favoured products start playing an increasingly important role on coking. Moreover, the retention of the coke formed at high temperatures is mainly due to steric blockage in the pores and/or cavities and only a few molecules remain trapped owing to their low volatility.

Coke composition is deeply affected by temperature and, at low temperatures, also by the nature of the reactant. In the case of paraffinic or olefinic hydrocarbons, coke consists of branched oligomers or naphthenic compounds, and the degree of substitution of the oligomers depends very much on the pore structure of the zeolite (oligomers formed on HY are more branched than those formed on HMOR and on HZSM-5). Coke formed from alkylaromatics consists of polynuclear compounds originating from condensation reactions through benzilic cations and diarilmethane compounds as intermediates. At high temperatures, independently of the nature of the reactant, coke is formed by polynuclear aromatic compounds whose dimensions depend on the zeolite pore structure. The gradual formation of dichloromethane insoluble compounds (insoluble coke) as reaction temperature or coke content increases is also observed.

Both the acid characteristics and the pore structure of the zeolite play a significant role during coking. These parameters influence the reactions related to coke formation

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as well as its retention. Thus, the stronger the acid sites, the faster the reactions and the slower the diffusion rate of the intermediates with basic character, and hence, the greater the rate of coke formation. The density of acid sites has also a positive effect on coking, since the latter is associated to bimolecular reactions occurring in series. The influence of the available space near the active acid sites is somewhat complex: the smaller this space the stronger the sterical constraints for the formation of the bulky intermediates associated to coke (negative effect) but the greater the effect of concentration (a marked positive effect in bimolecular reactions). However, at high reaction temperatures, the main effect of the pore structure is related to the retention of coke molecules inside the pores. The greater the difference between the size of the cavities (or pore intersections) and the pore apertures the more difficult is the diffusion outwards of the large coke molecules so formed. The final amount of coke in each zeolite is also dependent on the space available inside the pores and/or cavities of the zeolite (9). Another parameter which plays a significant role on coke composition and specially on its deactivation effect (15) is the mode of diffusion of reactants and products in the pores: either tridirectional as in Y and ZSM-5 zeolites or monodirectional as in mordenite. However, hydrothermal and/or acid treatments can create mesopores which change the mode of diffusion from mono to tridirectional significantly, improving zeolite stability (15).

In this work the formation of coke was investigated during *o*-xylene transformation at various temperatures over two H-mordenites differing by their acidity and their pore structure. The first one resulted from simple calcination of a NH_4-mordenite sample, whereas the second one resulted from hydrothermal and acid treatments of this sample. The choice of *o*-xylene transformation as a model reaction is justified by the fact that mordenite catalysts are commercially used in the isomerization of the C8 aromatic cut (16). Despite the industrial interest in mordenites there are but a few reports on coking over this zeolite and data on coke composition for this monodimensional porous network can only be found for *n*-heptane at 723 K (1). Most of the work done in this field refers to USHY and HZSM-5, whose pore structures are markedly different from that of mordenite.

2. EXPERIMENTAL

2.1. Sample Preparation

The parent sample was a commercial Na mordenite (Zeolon 900Na—PQ Corporation) (NaMZ). The original grains (1.0 mm average diameter) were ground to $-65+150$ mesh Tyler. It was ion exchanged with a 2M NH_4Cl solution ($NH_4/Na = 5.0$) at room temperature. The ammonium form was either calcined under dry air at 823 K, for 2 h (sample HMA) or submitted to two cycles of hydrothermal/acid treatments (sample HMB). The hydrothermal treatments were performed in a tubular furnace under 20 g/h of 100% steam at 823 K for 2 h and the acid treatments with a 4M HCl solution under reflux for 2 h and a ratio of 30 ml of acid per gram of zeolite.

2.2. Reaction Conditions

The coked samples were obtained by feeding *o*-xylene to a fixed-bed micro-reactor; *o*-xylene was previously shown to be the isomer with the largest tendency to deactivate acid mordenite (9). The influence of reaction temperature was evaluated at atmospheric pressure, under H_2 at 523, 623, and 723 K. The molar ratio $H_2/o\text{-}X$ was always equal to 6 ($o\text{-}X$ partial pressure = 0.15 bar). The values of WHSV (gram of xylene per hour per gram of catalyst), 50 h^{-1} for HMA and 100 h^{-1} for HMB, so selected as to give similar initial conversions at each temperature, were kept constant in all the experimental runs. Reaction products analysis was performed by gas chromatography on a 8.5-m di-*n*-decylphtalate/bentone 34 on Chromosorb P packed column with a thermal conductivity detector. At the end of a run, the coked sample was always kept under N_2 for 30 min at the reaction temperature, before being cooled down to room temperature also under N_2.

2.3. Characterization

The chemical composition of the zeolite samples was measured by X-ray fluorescence (XRF). Solid state Si^{29} and Al^{27} NMR spectra were used for determination of framework composition and also of the presence of framework defects (silanol groups) and extra-framework aluminium species (EFAL). Surface composition was measured by X-ray photoelectron spectroscopy (XPS). Textural properties were determined by N_2 adsorption while density and strength of acid sites were measured by NH_3 thermodesorption analysis (NH_3 TPD). The crystallinity of the samples was determined by X-ray diffraction (XRD). More details were given by Fernandes *et al.* (17).

The coke content of the samples was determined by a LECO analyser.

For the chemical identification of coke, the methodology developed by Magnoux (2) was used. The coked sample was treated with an HF solution at room temperature to dissolve the zeolite and to liberate the coke. The soluble components of coke were next extracted with dichloromethane (CH_2Cl_2) and analysed by GCMS and HNMR. The yield (Y) was defined as the fraction (weight basis) of the total coke that could be extracted with dichloromethane.

For temperature programmed oxidation (TPO) analysis the coked samples were initially dried under N_2 flow up to 473 K at 7 K/min. Next, the coke was burnt under a 2.6% O_2/He mixture up to 1173 K at 7 K/min.

3. RESULTS AND DISCUSSION

3.1. Physico–Chemical Characteristics of the Samples

The samples used in this work presented marked differences in their acidic and textural characteristics which significantly influenced coke formation. The overall, the lattice and the external surface SAR (SiO_2 to Al_2O_3 ratio), along with the main acidic and textural characteristics of the samples are listed in Table 1. The sodium content (percentage of Na_2O) of the dealuminated samples was less than 0.3%.

Even for sample HMA, calcined under dry air, there was a significant dealumination most likely due to self-steaming. Indeed Al^{27} MAS/NMR analysis indicated that at least 17% of the total Al was in the form of extra framework species with octahedral coordination. The SAR determined by Si^{29} MAS/NMR, somewhat greater than that measured by Al^{27} MAS/NMR, could be attributed to the presence of NMR "invisible" EFAL, even after ACAC (acetylacetone) impregnation. These EFAL species, strongly resistant to ACAC impregnation, were probably situated inside the secondary channels of mordenite, making it difficult for ACAC to access them (18).

For sample HMB, the two cycles of steaming/acid leaching produced, as expected, a significant framework dealumination. About 12% of the total Al was present as octahedrally coordinated EFAL. The incomplete leaching of EFAL was previously reported (17) for samples treated at similar conditions.

TPD of NH_3 showed a decrease in acid site density with decreasing structural Al content and a relative increase in the strength of the acid sites (see Table 1) as a consequence of the reduction of the interacting forces between acid sites (19).

TABLE 1

Composition, Acidic, and Textural Properties of the Samples

	NaMZ	HMA	HMB
SAR			
Chemical—XRF	10.9	10.9	65.8
Framework—Si^{29} MAS/NMR	9.2	15.4	—
Framework—Al^{27} MAS/NMR	10.9	13.2	74.5
Surface—XPS	—	12.0	54.8
Total acidity (μmol/g)[a]	—	956.7	129.4
Strong acidity (μmol/g)[b]	—	531.9	96.3
S_{BET} (m^2/g)	327	441	469
$V_{micropores}$ (cm^3/g)[c]	0.129	0.175	0.197
$V_{mesopores}$ (cm^3/g)[d]	0.022	0.031	0.125
Crystallinity (XRD)	91	92	157

[a] TPD NH_3.
[b] NH_3 desorbed above 623 K.
[c] *t*-Plot.
[d] BJH (20–600 Å).

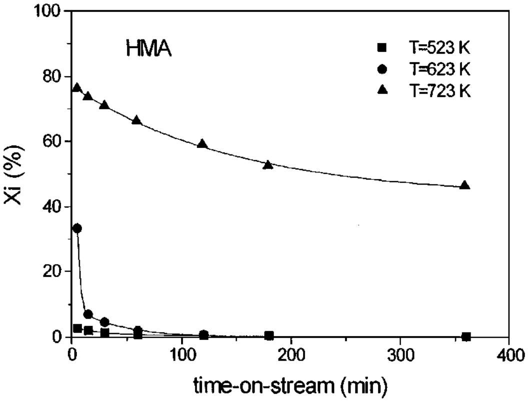


FIG. 1. *o*-Xylene isomerization conversion over HMA. Conversion vs time-on-stream at various temperatures.

Dealumination also led to changes in textural characteristics. Sample HMA showed an increase in BET specific area and in micropore volume when compared to the parent sample. This reflects the removal, during the ionic exchange step, of the species left behind in the zeolite channels after synthesis. However, micropore volume for this sample was still somewhat low due to partial pore blockage by the EFAL produced during calcination.

The two steaming/leaching cycles generated a significant mesopore volume in sample HMB. Most of those mesopores were about 30–50 Å in diameter and should create an effective communication between the channels of mordenite, thus reducing its diffusional restraints. Also, the crystalline structure of this sample was preserved as indicated by the micropore volume.

The crystallinity of the samples correlates well with the observed micropore volume and its variation with different calcination conditions has been previously discussed (17).

3.2. Catalytic Activity

o-Xylene isomerization was strongly temperature dependent. At 523 K, low conversions were observed on both mordenite samples, *m*-xylene being virtually the only product. At 623 and 723 K disproportionation was also observed as a secondary reaction and the product stream contained all xylene isomers, toluene, and trimethylbenzenes.

Figures 1 and 2 show isomerization conversion (defined as $(1 - y) \times 100$, y being the molar fraction of *o*-xylene among the xylene isomers in the exit stream) as a function of time on stream at different temperatures for samples HMA and HMB, respectively. Increasing the temperature, as expected, also increased the deactivation rate of both samples, especially of sample HMA, due to its sensitivity to pore blockage. Deactivation coefficients according to the Voorhies equation (20) are given in Table 2. At 723 K isomerization equilibrium conversions were attained over sample HMB and deactivation rates could not be measured.

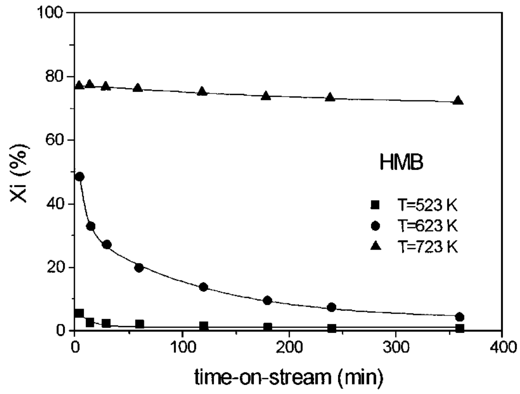


FIG. 2. *o*-Xylene isomerization conversion over HMB. Conversion vs time-on-stream at various temperatures.

Apparently the mesoporous system of sample HMB, which reduced the constraints to the access of the reagents to the active sites, made it more active than sample HMA, despite the higher acid site density of the latter. Also, this secondary mesoporous system, interconnecting its main channels and decreasing its susceptibility to blockage by coke, along with its lower acid sites density, made sample HMB more resistant to deactivation. Therefore the higher initial activity of HMB could be due to an extremely rapid deactivation of HMA acid sites during the first few minutes of the reaction (i.e., before the first activity measurement).

3.3. *Coke Formation*

In all cases coke formation was observed along the reaction. Table 3 shows total coke contents and soluble coke yields. At 623 K the amounts of coke at the end of the runs should correspond to the limiting value for each case, since the remaining activity was extremely low.

It can be observed that for similar reaction times and temperatures, the amount of coke deposited on HMB is larger than that on HMA. Provided mass transfer effects are absent, one does not expect that the different flow rates used should have a large influence on the coking rate. So, the behavior of the two samples may be explained by taking into account both the acidic and textural properties of the zeolites. As far as acidity is concerned, coking is favoured by higher acid site density and strength. On the other hand, larger pores and/or cavities can hold larger amounts of coke.

So, for sample HMA the high concentration of acid sites would be responsible for a rapid coking rate close to the pore mouth. Along with the absence of a mesoporous system and the presence in the pores of the EFAL generated during calcination, this would lead to pore blockage, fast deactivation, and limited room for coke deposition.

TABLE 2

Deactivation Coefficients (*n* from Voorhies Eq. (20)) for *o*-Xylene Isomerization

T (K)	HMA	HMB
523	0.57	0.48
623	0.96	0.65

TABLE 3

Coke Contents (Total, Soluble, and Insoluble in CH_2Cl_2) and CH_2Cl_2 Extraction Yields (*Y*)

Sample	*T* (K)	*t* (min)	%C_{total}	%C_{sol}	%C_{insol}	*Y* (%)
HMA	523	360	2.9	2.9	0	100
	623	20	2.1	2.0	0.1	95
		360	2.2	2.0	0.2	90
	723	20	1.9	0.6	1.3	35
		360	2.1	0.6	1.5	30
HMB	523	30	4.3	4.3	0	100
		360	4.1	4.1	0	100
	623	30	2.5	2.2	0.3	90
		360	5.0	2.5	2.5	50
	723	30	4.6	1.1	3.5	25
		360	5.4	0.5	4.9	10

For sample HMB the mesoporous system would allow the access of the reactants even to sites within pores whose entrances were blocked and would also provide additional space for coke accommodation. Accordingly, the final coke content of this sample was much larger and the deactivation rate lower than that of sample HMA. These facts clearly show that the presence of mesopores interconnecting the main channels of mordenite reduces significantly the coke toxicity.

Also, for sample HMB it was possible to observe an interesting behaviour of the total amount of coke after 30 min of reaction as a function of temperature. At 523 K, the formation of relatively low molecular weight CH_2Cl_2 soluble molecules is rapid and they remain trapped in the zeolite porous system. As temperature is increased the more volatile molecules can no longer be retained in the pores and the kinetics of their transformation into longer chain molecules is still slow. As a consequence, the total amount of coke goes through a minimum yet most of it still soluble. Finally, at 723 K, heavier molecules are rapidly formed and the total amount of coke increases again, now most of it being CH_2Cl_2 insoluble. Such behaviour could not be observed for zeolite HMA since the limiting coke amounts were rapidly attained.

The final colour of the samples was dependent on the temperature, coking extent, and coke distribution in the particles. The coked HMA samples were always darker than the corresponding HMB ones, as a consequence of preferential coke deposition on the external surface of the former. All the samples were darker the higher the temperature or the coke content. So, all HMA samples were black except that coked at 523 K which was grey. Sample HMB coked at 523 K was light grey after 20 min and brown after 6 h.

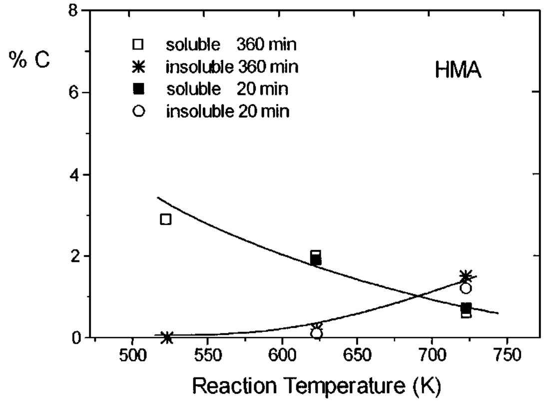


FIG. 3. Soluble and insoluble coke formed on HMA at different reaction temperatures.

HMB samples coked at both 623 and 723 K were dark grey and black after 30 min and 6 h, respectively.

The variation of both soluble and insoluble coke contents with temperature and time for samples HMA and HMB is shown in Figs. 3 and 4. It can be seen that increasing the temperature favoured the transformation of soluble coke into insoluble coke. In all cases, the amount of insoluble coke increased with increasing temperature while the amount of soluble coke showed an opposite behaviour. At 523 K, all the coke was soluble for both samples and both reaction times. Those results agree with others previously reported (2, 4, 6, 8, 11, 12, 21), indicating that temperature has a positive effect on the formation of dichloromethane insoluble species, even when the total amount of coke does not change appreciably. For sample HMA at both 623 and 723 K the soluble coke content seems to have reached a limiting value after 20 min of reaction. From then on, a slight increase, if any, in the amount of insoluble coke is observed.

For sample HMB, the amount of soluble coke also seems to nearly reach a limiting value after 30 min. For the lower temperature, since there is no formation of insoluble coke, this also corresponds to the total amount of coke. On the other hand, at 623 and 723 K there is a marked increase of insoluble coke content with time, although this effect is less pronounced at 723 K, since at this temperature the transformation of soluble coke in insoluble coke is fast. The high contents of insoluble coke on both samples at 723 K are in accordance with the results of Guisnet and Magnoux (1) for *n*-heptane at 723 K, which showed that the formation of insoluble coke is strongly favoured over mordenite as compared to other zeolites (USHY, HZSM-5, and H-erionite).

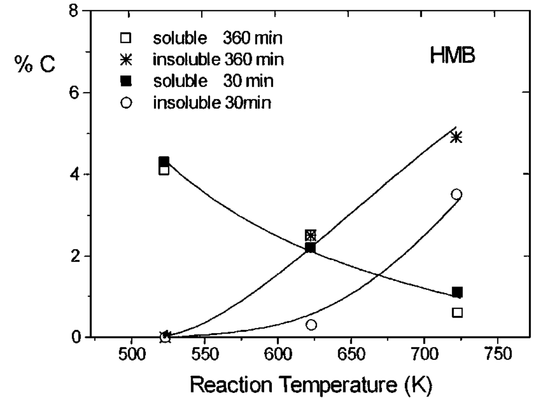


FIG. 4. Soluble and insoluble coke formed on HMB at different reaction temperatures.

At 623 and 723 K, after 360 min time-on-stream, the extraction yields for HMB were much lower than those for HMA. This is a direct consequence of the larger amounts of coke observed for HMB, since it has been previously shown that the extraction yield decreases with increasing coke content (1, 9, 11, 12).

The comparison between V_C (volume occupied by coke molecules, estimated according to Magnoux *et al.* (7)) and V_P (micro plus mesopore volume) shows that only a small part of the zeolite pore volume is occupied by coke, even for samples which are virtually inactive, as can be seen in Table 4. This result agrees with those previously reported (1), ascribing the deactivation of mordenites mainly to pore blockage.

Table 4 also shows the comparison between the number of coke molecules, N_C (the average molecular weight of the soluble fraction was estimated from coke composition and that of the insoluble fraction as in Ref. (7)) and the number of acid sites, N_A (based on framework Al contents). The low values of the ratio N_C/N_A for sample HMA reinforce the observation that for mordenites deactivation is by pore mouth blockage. For HMB, as already pointed out, the presence of mesopores allowed the access of *o*-xylene to a relatively larger number of sites and the accommodation of much more coke.

As the temperature increases the N_C/N_A ratio decreases for both samples, mainly due to the increase of the average coke molecular weight (Figs. 5 and 7 and (3.4)). That is to say, coke toxicity increases as temperature is raised.

The data at 723 K were not used for those comparisons since the zeolites were still very active after 360 min TOS and also because the uncertainties in the determination

TABLE 4

V_C/V_P and N_C/N_A Ratios for HMA and HMB Samples after 360 min TOS

Sample	*T* (K)	V_C/V_P	N_C/N_A
HMA	523	0.11	0.05
	623	0.08	0.03
HMB	523	0.10	0.40
	623	0.10	0.25

Note. V_C = volume occupied by coke; V_P = volume of micro + mesopores; N_C = number of coke molecules; N_A = number of acid sites.

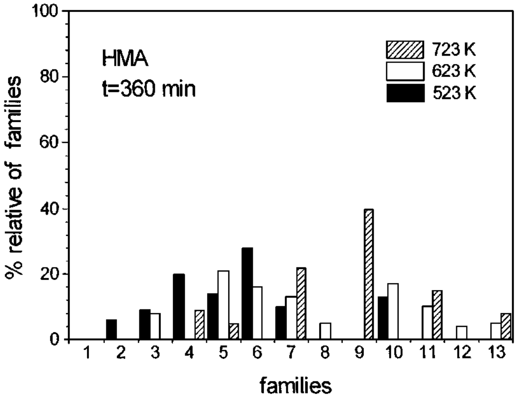


FIG. 5. Distribution of the families present on soluble coke (HMA—360 min).

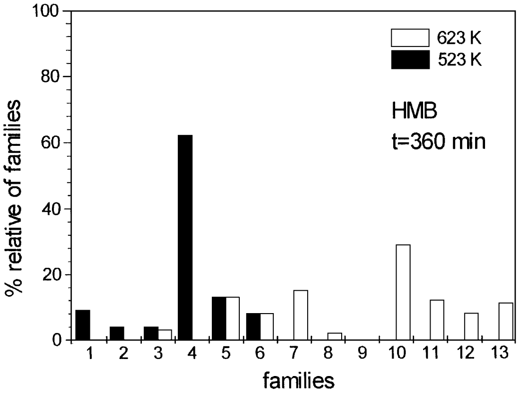


FIG. 7. Distribution of the families present on soluble coke (HMB—360 min).

of the average molecular weight of the insoluble fraction would now be a major drawback, since at this temperature most of the coke was insoluble.

3.4. Coke Characterization

The soluble coke components were classified in families of general formula C_nH_{2n-z}. Within each family the differences in molecular weight were multiples of 14, corresponding to substituting a methyl group for a hydrogen atom.

Table 5 presents the molecular formula and the most probable structural formula for these families, the number of unsaturated bonds plus cycles (Un + Cy), the range of molecular weights found and the approximate boiling points and dimensions of the molecules. The number of unsaturated bonds plus cycles is given by $\mathrm{Un}+\mathrm{Cy}=z/2+1$ and is representative of the aromaticity of a given family.

Semiquantitative estimates of the distribution of the families in the soluble fraction were made from the height of the peaks of the components of each family in the mass spectra, as illustrated in Figs. 5 to 7. It can be observed that the temperature, besides affecting significantly the global coke composition, also has an important effect on the composition of the soluble fraction. The very low extraction yields for HMB coked for 360 min at 723 K did not allow a precise composition evaluation.

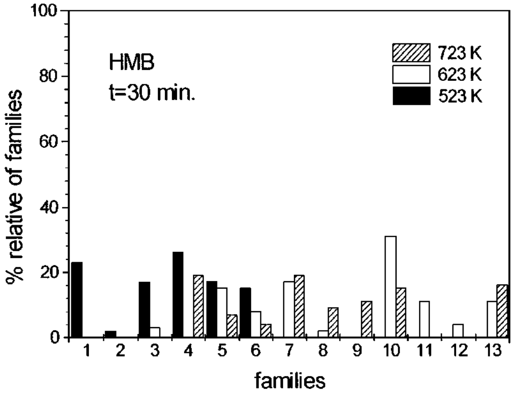


FIG. 6. Distribution of the families present on soluble coke (HMB—30 min).

At 523 K, on HMA, family C_nH_{2n-18} (6) was the main one followed successively by families C_nH_{2n-14} (4), C_nH_{2n-16} (5), C_nH_{2n-28} (10), and C_nH_{2n-22} (7). On HMB, family C_nH_{2n-14} (4) was the most important and families C_nH_{2n-16} (5) and C_nH_{2n-18} (6) were the next. For this sample, family C_nH_{2n-6} (1) was detected, particularly at low reaction times, corresponding to compounds originating from disproportionation reactions (tetra, penta, and hexa methylbenzenes). For both samples, at this temperature, tetrahydronaphtalene-type (C_nH_{2n-8}) (2) and naphtalene-type (C_nH_{2n-12}) (3) compounds were also formed.

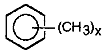
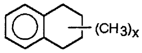
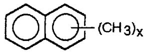
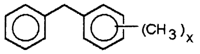
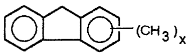
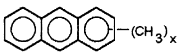
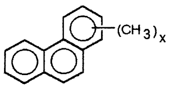
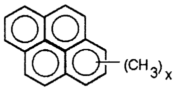
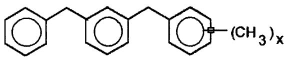
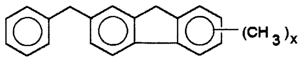
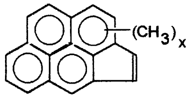
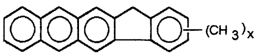
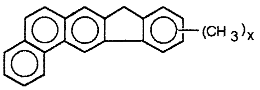
Raising the temperature to 623 K increased the contribution of the more "aromatic" families (C_nH_{2n-22} (7), C_nH_{2n-28} (10), and C_nH_{2n-32} (11), over HMA and C_nH_{2n-22} (7), C_nH_{2n-28} (10), C_nH_{2n-32} (11), and C_nH_{2n-38} (13) over HMB) and the C_nH_{2n-14} (4) products were no longer detected. For the two samples, the distribution of the families was roughly the same for both reaction times.

At 723 K most of the coke was insoluble (the insoluble fraction consisted of small black aggregates of highly condensed polynuclear aromatic compounds). A new family (C_nH_{2n-26}) (9) appeared in the soluble fraction, besides families C_nH_{2n-22} (7), C_nH_{2n-32} (11), and C_nH_{2n-14} (4) for HMA and C_nH_{2n-22} (7), C_nH_{2n-28} (10), and C_nH_{2n-38} (13) for HMB, and no significant increase in the contribution of the more "aromatic" families was observed for longer reaction times.

H-NMR analyses confirmed that coke aromaticity increased with temperature. Figure 8 is an example of the influence of this parameter on the ratio between aromatic (H_{AR}, 7 ppm $\leq \delta \leq$ 9 ppm) and alkylaromatic (H_{AA}, 2 ppm $\leq \delta \leq$ 3 ppm) protons. As for time-on-stream, its influence on coke aromaticity was minor. For samples coked at 623 and 723 K this is in accordance with the previously

TABLE 5

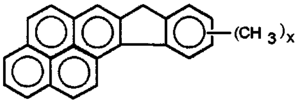
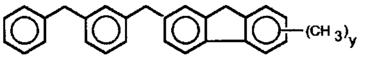
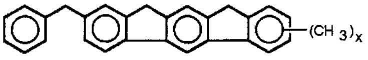
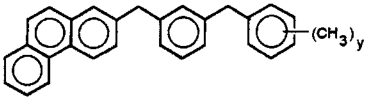
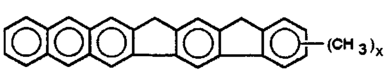
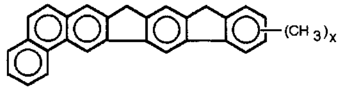
Main Components of the CH_2Cl_2—Soluble Coke Fraction

Family	Structural Formula		Molecular Formula	Un + Cy	Molecular Weight	B.P. (K)	Size (Å)
1		$4 \leq x \leq 6$	C_nH_{2n-6}	4	134 - 162	468-538	
2		$2 \leq x \leq 4$	C_nH_{2n-8}	5	160-188	> 479	(6.0 x 7.0)
3		$2 \leq x \leq 4$	C_nH_{2n-12}	7	156-184	> 493	(6.0 x 7.0)
4		$2 \leq x \leq 7$	C_nH_{2n-14}	8	196 - 266	583	(6.0 x 9.5)
5		$0 \leq x \leq 7$	C_nH_{2n-16}	9	166 - 264	588	(6.0 x 9.5)
6	 or 	$0 \leq x \leq 4$	C_nH_{2n-18}	10	178 - 234	633 613	(6.0 x 9.5) (6.0 x 8.5)
7	7a 	$0 \leq x \leq 5$	C_nH_{2n-22}	12	202 - 272	> 668	(8.0 x 8.5)
	7b 	$2 \leq x \leq 4$			286 - 314	> 633	(6.0 x 15.5)
8		$0 \leq x \leq 5$	C_nH_{2n-24}	13	256-326		(6.0 x 15.5)
9		$0 \leq x \leq 5$	C_nH_{2n-26}	14	226 - 296	> 723	(8.5 x 9.5)
10	 or 	$0 \leq x \leq 6$	C_nH_{2n-28}	15	266 - 350	> 673 > 673	(6.0 x 15.5) (6.0 x 14.0)

mentioned similarity of the families distribution for 30 and 360 min. On the other hand, data for HMB at 523 K indicated that, although the composition of the families varied, this variation was such as to keep the average aromaticity nearly constant. Magnoux *et al.* (11) reported the influence of the temperature and coke content on the aromaticity of the coke obtained from toluene over USHY. Our results agree with theirs as far as the temperature is concerned. However, the influence of coke content could not be clearly pointed out, possibly due to the fast coking rate on mordenite.

The structural formulas displayed in Table 5 show that most of the molecules are roughly linear, fitting the pseudo monodimensional porous structure of mordenite which limits the growth of coke molecules to the axial direction of the pores. Despite this geometric effect, the comparison of our

TABLE 5—*Continued*

Family	Structural Formula	Molecular Formula	Un + Cy	Molecular Weight	B.P (K)	Size (Å)
11	11a  0 ≤ x ≤ 3	C_nH_{2n-32}	17	290 - 332	> 723	(8.0 x 13.0)
	11b 				> 723	(6.0 x 21.5)
12		C_nH_{2n-34}	18	344-386	> 723	(6.0 x 21.5)
	or  0 ≤ x ≤ 3				> 723	(8.0 x 19.0)
13		C_nH_{2n-38}	20	354 - 438	> 723	(8.0 x 19.0)
	or  0 ≤ x ≤ 6				> 723	(6.0 x 21.5)

results with those reported by Magnoux *et al.* (11) for coke formed from toluene over USHY at different temperatures shows that some of the families were the same in both cases. This is indicative that the same mechanism is operative from o-xylene and toluene, going through diarylmethane-type compounds as intermediates. Those authors have presented a detailed discussion on how those families are formed. A simplified scheme can be seen in Fig. 9.

The reason why coke molecules remained trapped in the porous structure of the mordenites varied with temperature. At 523 K the main products have boiling points above the reaction temperature and would be retained due to both their strong absorption and low volatility. At the higher temperatures (623 and 723 K), besides the low volatility, the size of the molecules, close to the pore dimensions, would be responsible for their retention. Compounds with boiling points below the reaction temperature were also detected as, for example, C_nH_{2n-16} at 623 K and C_nH_{2n-14} at 723 K. Most probably they remained trapped by larger molecules (insoluble coke) which blocked the pores, not allowing the small molecules to leave the structure or to grow to larger ones. Such results were not observed over USHY (11), probably due to its tridimensional porous structure which reduces the probability of such a blockage.

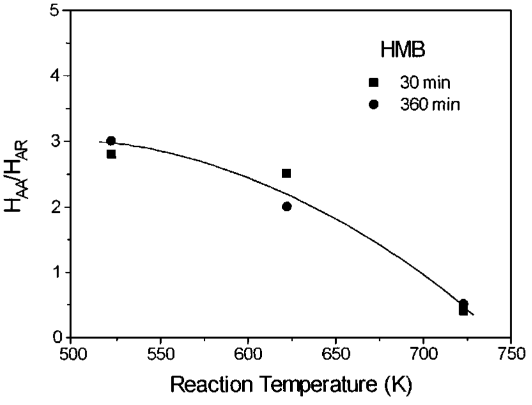


FIG. 8. HNMR HAA/HAR ratio for HMB.

3.5. *Coke Combustion*

Three of the samples coked at 623 K were submitted to temperature-programmed oxidation (TPO). Samples were selected, taking into account differences in acid and textural characteristics of the zeolites as well as differences in the extension of coking. Samples HMA (360 min), HMB (30 min) and HMB (360 min) were so chosen.

Figure 10 shows that the profiles of coke combustion are hardly affected by the total amount of coke. Curves (b) and (c) refer to samples with large differences in both coke

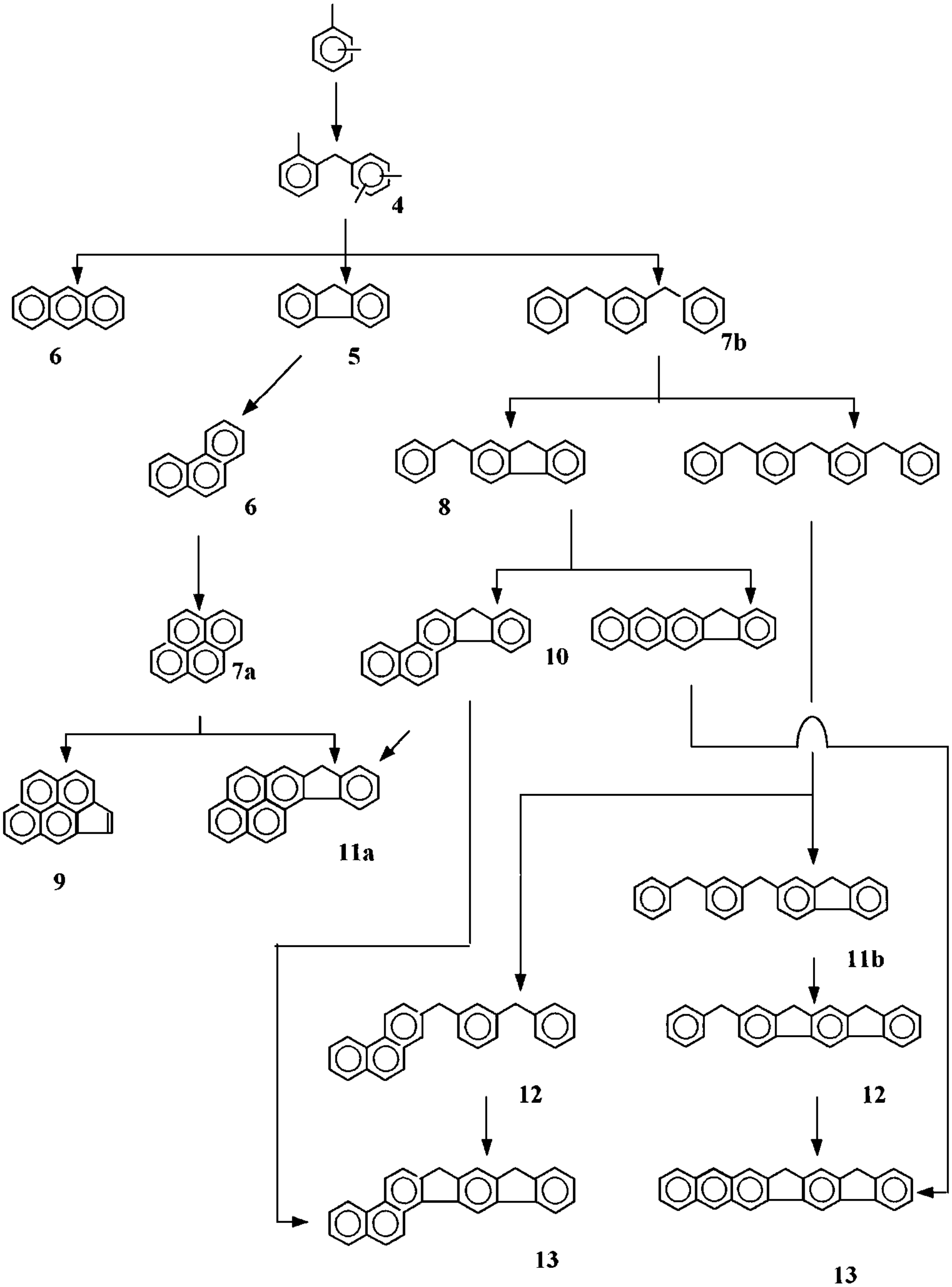


FIG. 9. Simplified reaction scheme for coke formation from *o*-xylene.

content and extraction yields. Yet, the temperature range for oxidation and the temperature for maximum CO_2 production are roughly the same for the two samples. One could have expected that the combustion of insoluble coke should require more severe conditions, but this was not observed.

On the other hand, curves (a) and (b) of Fig. 10 show different combustion behaviour for similar coke contents over different mordenites, although the initial oxidation temperature is about the same. Both the final temperature for complete oxidation and the temperature for maximum CO_2 production are lower for HMA than for HMB. Although differences in porous structure could affect the rate of combustion (22), recent results of Moljord *et al.* (23) show that the density of acid sites is generally the more important factor in determining the rate of coke oxidation over acid zeolites. The larger the number of Al atoms or protonic sites per unit cell, the smaller the fraction of total coke which requires high temperature to burn. The present results support this proposition. The higher temperatures required for

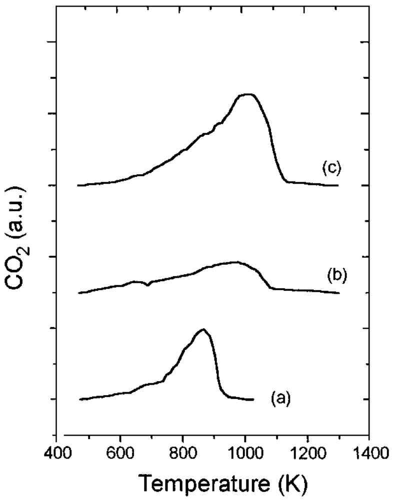


FIG. 10. Coke oxidation on different zeolites and total coke contents: (a) HMA, 360 min, %C = 2.2%; (b) HMB, 30 min, %C = 2.5%; (c) HMB, 360 min, %C = 5%.

coke burning over sample HMB reflect its lower acid site density.

4. CONCLUSIONS

The coking of two acid mordenites with *o*-xylene was investigated during *o*-xylene transformation at temperatures between 523 and 723 K. For the more dealuminated sample (HMB), mesopores interconnect the main channels, thus favoring the diffusion of reactant molecules towards active sites and increasing the space available for coke formation. Therefore, despite its lower acid site density, this sample is apparently more active than the slightly dealuminated sample (HMA) for *o*-xylene transformation and especially much more resistant to deactivation.

The reaction temperature has a significant effect on coking, on coke composition, and on coke toxicity. The amount of insoluble coke increased with increasing temperature while the amount of soluble coke showed an opposite behaviour, supporting the proposition that insoluble coke molecules are formed from the soluble ones.

Coke that is soluble in CH_2Cl_2 is a complex mixture of polyaromatic compounds. The formation of these compounds most likely involves benzilic carbocations and diarylmethanes as intermediates. The composition of this soluble coke is significantly influenced by the reaction temperature. As the temperature increases, coke becomes gradually more aromatic but no significant influence of the reaction time on aromaticity was observed. At 523 K coke molecules (100% soluble in CH_2Cl_2) are retained in the pore structure due to their strong adsorption and low volatility, while at higher temperatures they are sterically blocked in the mordenite channels.

TPO analyses suggested that coke oxidation is roughly influenced by total coke content.

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