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m-Xylene Transformation over a USHY Zeolite at 523 and 723 K: Influence of Coke Deposits on Activity, Acidity, and Porosity

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The modes of coking and deactivation of a USHY zeolite during *m*-xylene transformation at 523 and 723 K were established. At both reactions temperatures, coke molecules result mainly from transformation of the diarylmethane intermediates of transmethylation reactions, olefinic products formed only at 723 K also participating in coke formation at this temperature. From the effect of the number of coke molecules on the accessible micropore volume, on the hydroxyl bands, and on the number of protonic sites able to retain adsorbed pyridine, it can be concluded that at both temperatures, deactivation is initially due to poisoning of the protonic sites, pore blockage by coke deposits appearing at longer time-on-stream. The effect of this latter mode of deactivation is more significant at 723 than at 523 K. No interaction of Lewis acid sites with coke molecules is observed, which suggests that these sites play no role in *m*-xylene transformation and coke formation. © 2000 Academic Press

Key Words: **USHY zeolite; *m*-xylene; coking; deactivation; coke composition; acidity; IR spectroscopy.**

INTRODUCTION

The effect on the hydroxyl groups of coke molecules formed at short time-on-stream on a USHY zeolite during *m*-xylene transformation at 523 and 723 K was previously reported (1). The most acidic ones, i.e., the bridging hydroxyls in interaction with extraframework aluminium species, were found to be the most affected whereas no interaction was observed between coke molecules and the nonacidic hydroxyls. Furthermore, pyridine adsorption was shown to provoke a decrease in coke content as well as in the intensity of the corresponding bands. It was therefore concluded that pyridine molecules could displace, at least at low coke contents, the molecules of coke adsorbed on the acid sites, making their diffusion in the micropores easier and hence their desorption from the zeolite crystallites.

In this paper, coking and deactivation of the USHY zeolite were investigated during the same reaction and at the same temperatures as a function of time-on-stream. The composition of coke was established for samples coked at various time-on-stream, hence containing different amounts of coke, through the method developed in our laboratory (2) and the number of coke molecules was estimated. The porosity of coked samples was characterized by nitrogen adsorption and their acidity by IR spectroscopy in the absence (OH bands) and in the presence of pyridine (number of protonic and Lewis sites adsorbing pyridine molecules). The large differences found for *m*-xylene transformation at 523 and 723 K in coke composition as well as in the effect of coke molecules on acidity and porosity will be explained.

EXPERIMENTAL

The USHY zeolite ($Na_{0.4}H_{29.6}[(AlO_2)_{30}(SiO_2)_{162}]$, with 22.7 extraframework aluminium atoms) was obtained by calcination of a NH_4Y zeolite (CBV 500, from PQ) under air flow at 773 K for 12 h. The porosity and acidity characteristics were previously reported as well as the conditions for *m*-xylene transformation ($p_{m\text{-xylene}} = 0.1$ bar, $p_{N_2} = 0.9$ bar) for product and coke analysis and for characterization of acidity by IR spectroscopy (1). Nitrogen adsorption measurements were performed at 77 K with the gas adsorption system ASAP 2000 (Micromeritics).

When all of the coke components can be identified (i.e., whatever the time-on-stream at 523 K and at short time-on-stream at 723 K), the number of coke molecules can be accurately estimated from coke content and composition. This is not the case for high coke contents at 723 K because part of the coke molecules, which are insoluble in methylene chloride, cannot be identified. A value of 600 $g \cdot mol^{-1}$ for the molecular weight of insoluble coke molecules was used for estimating their number. However, there was no change in the general effect of coke molecules when values of 500 or 700 were used instead of 600 $g \cdot mol^{-1}$.

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RESULTS

1. *Conversion of m-Xylene and Coke Formation*

At both temperatures, *m*-xylene undergoes two main reactions: isomerization (I) into *o*- and *p*-xylenes and disproportionation (D) into toluene and trimethylbenzenes. In addition, at 723 K, C_2–C_4 alkenes are also found at high conversions. Whatever the temperature and the contact time, a rapid deactivation of the catalyst is observed. However, the conversion on the fresh catalyst can be estimated by carrying out various analyses at short time-on-stream (TOS) values. As expected, *m*-xylene transformation is much faster (15–20 times initially) at 723 than at 523 K.

On the fresh catalyst, the isomerization selectivity is practically independent on conversion and temperature (p/o ratio close to 1.0). At 523 K, deactivation causes a decrease in the p/o ratio whereas at 723 K there is practically no effect. On the other hand, the disproportionation/isomerization ratio over the fresh zeolite increases with conversion and is practically independent of temperature. At 523 K, deactivation causes an increase of this D/I ratio (measured at identical conversions), whereas at 723 K, no effect is observed (Fig. 1). The deactivation is related to the retention of carbonaceous components on the zeolite ("coke"). The amount of coke was determined for various TOS values at a contact time τ of 0.065 h (τ is taken as the reverse of WHSV, the weight hourly space velocity). Figure 2 shows that the coke content of the zeolite first increases very rapidly with TOS and then is practically constant (at 523 K) or increases less rapidly (723 K). Whatever TOS, the amount of coke deposited is larger at 723 than at 523 K.

The effect of coke on *m*-xylene conversion is quite different at 523 and 723 K (Fig. 3). At 723 K the conversion decreases continuously as a function of coke content. At 523 K a change in coke content from 2 to 4.5 wt% (from 2 to 5 min) has practically no effect on *m*-xylene conversion whereas a further slight increase, from 4.5 to 6.0 wt%, causes a very pronounced decrease in conversion.

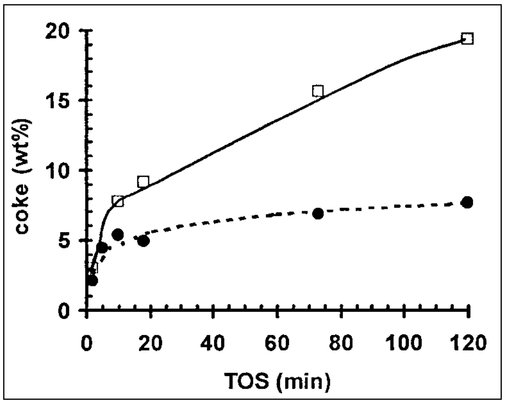


FIG. 2. Coke content on USHY samples vs time-on-stream at (●) 523 and (□) 723 K.

2. *Coke Composition*

For both temperatures, the composition of coke was determined at a contact time τ of 0.065 h through the technique developed in our laboratory, i.e., dissolution of the zeolite in hydrofluoric acid solution and recovering of coke molecules in two parts: one soluble in methylene chloride (CH_2Cl_2) and the other insoluble, hence constituted of very polyaromatic compounds (2). Practically no coke can be recovered through a simple soxhlet treatment of the coked zeolite samples; hence coke was essentially located within the pores.

At 523 K and whatever TOS, coke is completely soluble in CH_2Cl_2. At 2-min reaction (2.6 wt% coke), methyl-substituted anthracenic or phenanthrenic compounds (C_nH_{2n-18}) are the main coke components; methyl-substituted naphthalenic, pyrenic, and diphenyl methane

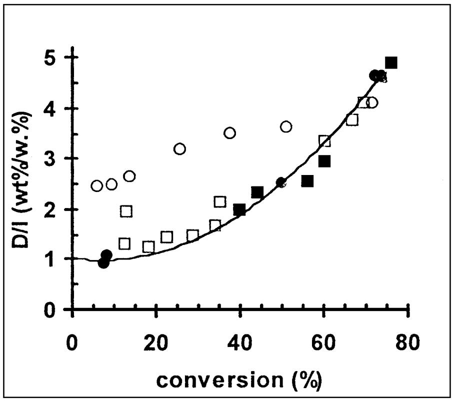


FIG. 1. Disproportionation to isomerization ratio (D/I) vs conversion at 523 K over (●) fresh and (○) deactivated USHY samples and at 723 K over (■) fresh and (□) deactivated USHY samples.

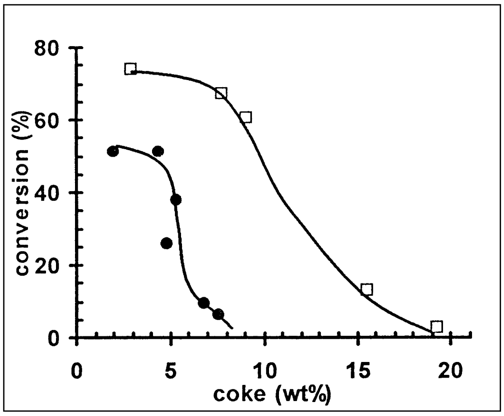


FIG. 3. Conversion of *m*-xylene vs coke content at (●) 523 and (□) 723 K.

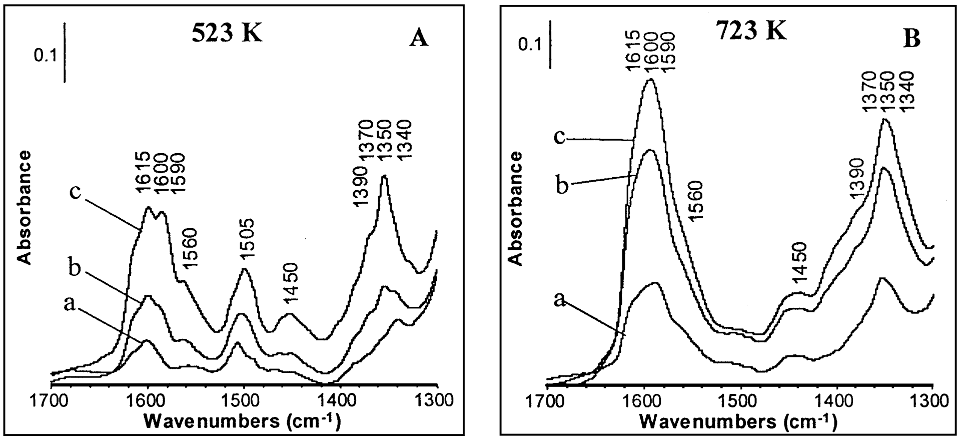
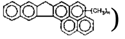


FIG. 4. IR spectra of the coked samples in the 1300- to 1700-cm^{-1} region at 523 K (A) for (a) TOS = 2 min, (b) TOS = 10 min, and (c) TOS = 73 min and at 723 K (B) for (a) TOS = 2 min, (b) TOS = 10 min, and (c) TOS = 18 min.

compounds are also present in relatively large amounts. The average number of aromatic rings in the coke components increases with TOS and hence with coke content as previously described (1). The chemical nature (methyl aromatic compounds) of coke components can be confirmed by IR spectroscopy of the coked samples. As was shown by other authors (3), the integrated absorbance of the bands in the 1655- to 1530-cm^{-1} region (Fig. 4) is proportional to the percentage of coke deposited on the zeolite.

The quantitative distribution of coke molecules estimated by GC is shown in Fig. 5 as a function of coke content. The components of C_nH_{2n-14} and C_nH_{2n-16} families were plotted together as also the bulkiest molecules (C_nH_{2n-22}, C_nH_{2n-28}, and C_nH_{2n-38}). The coke compounds which have the highest H/C ratio (the lightest) are directly formed (apparent primary products) whereas the bulkiest seem to result from the transformation of the primary products (Fig. 5). The secondary mode of formation of these latter products is shown not only by their appearance for coke contents higher than 3 wt% (Fig. 5B) but also by the maximum in the yield in primary coke components (Fig. 6A).

At 723 K coke is completely soluble in CH_2Cl_2 only for low coke contents (lower than 3 wt%). At higher coke contents, part of the coke is constituted of highly polyaromatic molecules which are insoluble in CH_2Cl_2 (Fig. 6).

Four families of components are found in the soluble coke: methyl derivatives of pyrene (C_nH_{2n-22}), of benzofluoranthene (C_nH_{2n-26}), of indenopyrene or dibenzochrysene (C_nH_{2n-32}), and bulkier aromatic compounds () with a C_nH_{2n-38} general formula. For a coke content of 3 wt%, methyl-substituted pyrenic compounds (C_nH_{2n-22}) are the main components (80%). At higher coke contents (e.g., 8.1 wt%), pyrenic components disappear at the benefit of more polyaromatic components. IR spectroscopy confirms that the coke formed at 723 K is more polyaromatic than the coke formed at 523 K. As was the case at 523 K, a proportionality is found between the integrated absorbance of the band at 1600 cm^{-1} and the percentage of

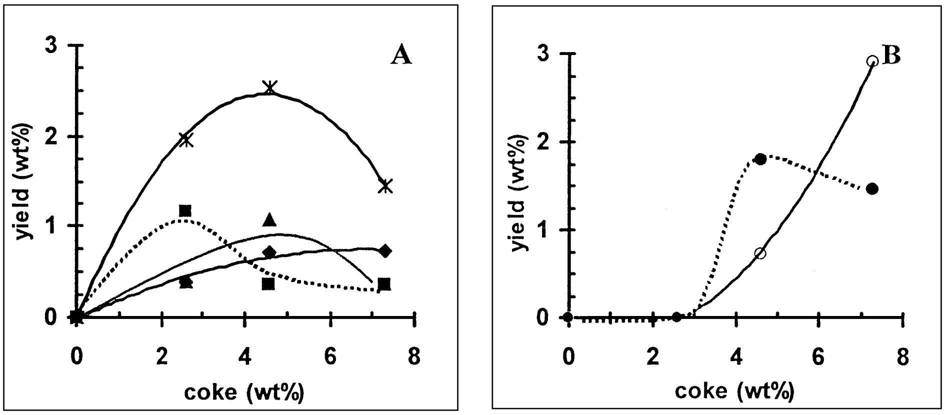


FIG. 5. Yield of the various families of coke formed at 523 K vs coke content. (A) Apparent primary products (◆) methylbenzene, (▲) methylnaphthalene, C_nH_{2n-12}, (■) $C_nH_{2n-14} + C_nH_{2n-16}$, and (✱) C_nH_{2n-18} and (B) secondary products (●) C_nH_{2n-20} and (○) $C_nH_{2n-22} + C_nH_{2n-28} + C_nH_{2n-38}$.

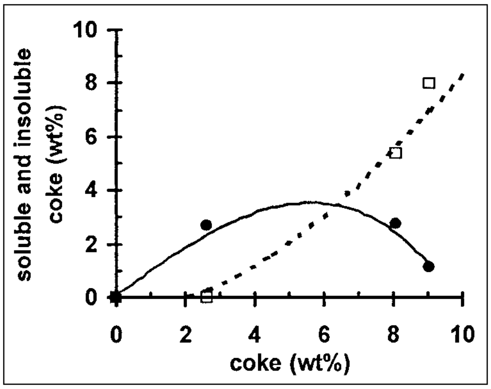


FIG. 6. Percentages (wt%) of (●) soluble coke in methylene chloride and of (□) insoluble coke formed at 723 K vs total coke content.

coke deposited on the zeolite. However, the ratio between these two values is higher at 723 than at 523 K, confirming differences in the polyaromaticity of the coke components.

3. *Influence of Coke on Pore Volume and Acidity*

The effect of coke on the micropore volume accessible to nitrogen is more significant for coking at 523 than at 723 K (Fig. 7A). From these results, the amount of coke causing a total blockage (V/Vo = 0) of the access to the ultramicropore (4) volume was estimated (linear extrapolation of the data in Fig. 7A) to be about 14 and 22 wt% for coking temperatures of 523 and 723 K, respectively. It should also be noted that the supermicropores (4) and the mesopores (4) are not affected by coke formed at 723 K and slightly affected by coke formed at 523 K (Fig. 7B).

The spectra of all of the hydroxyl groups, of those interacting (called acidic) and noninteracting with pyridine (e.g., nonacidic or nonaccessible by pyridine molecules), were previously shown (1). Seven bands are observed in the spectrum of acidic hydroxyls: 3550- and 3625-cm^{-1} bands were assigned to hydroxyls located in sodalite cages and in supercages, respectively, 3525- and 3600-cm^{-1} bands to the same type of hydroxyls in interaction with extraframework Al, a 3740-cm^{-1} band to silanol groups, and the other bands at 3665 and 3780 cm^{-1} to extraframework species (5–7).

Whatever the reaction temperature, coke molecules cause a decrease in the intensity of all of the acidic hydroxyl bands. However, as shown in Fig. 8 by the change with the coke content in the ratio between the intensities of the bands for the coked and the fresh samples, the bands at 3525 and 3600 cm^{-1} which correspond to the strongest acid sites are the most affected. This was previously shown by Vimont *et al.* (8). On the other hand, the IR bands of hydroxyl groups noninteracting with pyridine are practically not affected by coke deposits.

It should be emphasised that for low coke contents pyridine adsorption results in a decrease of the IR bands corresponding to coke molecules. This decrease, which is more pronounced for coking at 523 K, was previously explained by removal of coke. Pyridine molecules displace the weakly basic coke molecules from the acid sites, making possible their desorption by vacuum treatment (1).

The concentrations of Brønsted and of Lewis sites on the coked samples were determined from the intensity after desorption at 423 K of the bands corresponding to pyridinium ions (at 1545 cm^{-1}) and to pyridine bonded to Lewis acid sites (1450 cm^{-1}) by using the extinction coefficients previously determined (9). Figure 9A shows that the effect of coke on N_{H^+}, the number of protonic sites able to retain pyridine adsorbed at 423 K, is practically independent of the coking temperature. However, at 523 K, when the amount of coke increases from 4.5 to 6.0 wt%, a large decrease in N_{H^+} is observed. As various experiments were carried out in this range of coke contents (Fig. 9A), this curious decrease cannot be ascribed to experimental problems. Moreover, this decrease can be related to the strong decrease in *m*-xylene conversion (Fig. 3) observed in the

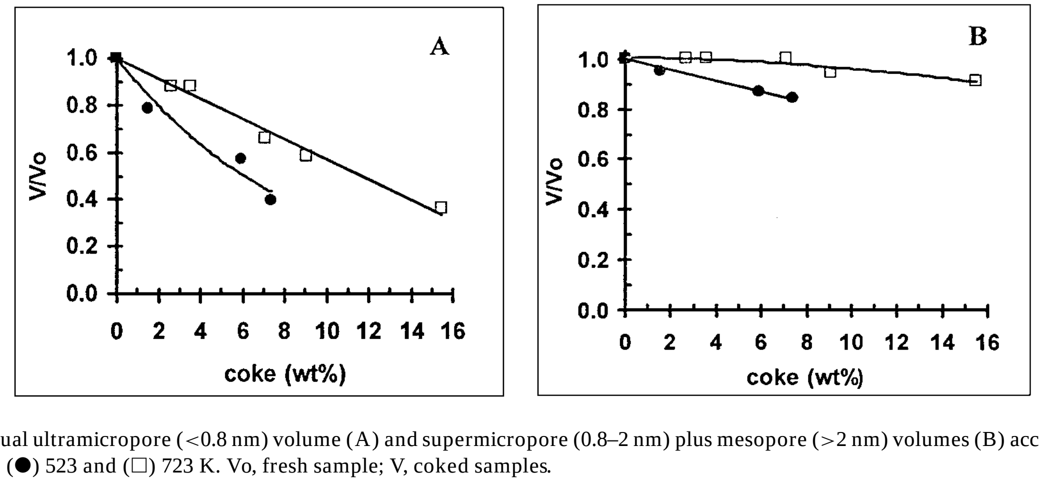


FIG. 7. Residual ultramicropore (<0.8 nm) volume (A) and supermicropore (0.8–2 nm) plus mesopore (>2 nm) volumes (B) accessible to nitrogen vs coke content at (●) 523 and (□) 723 K. Vo, fresh sample; V, coked samples.

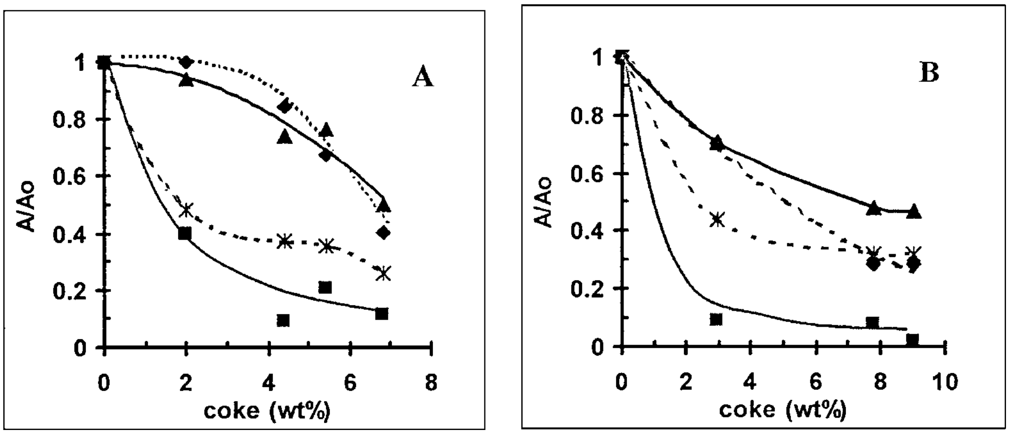


FIG. 8. Residual intensity of different OH bands vs coke content at 523 (A) and 723 K (B): (◆) 3625, (■) 3600, (▲) 3550, and (✱) 3525 cm^{-1}. Ao, integrated absorbance for the fresh sample; A, integrated absorbance for the coked samples.

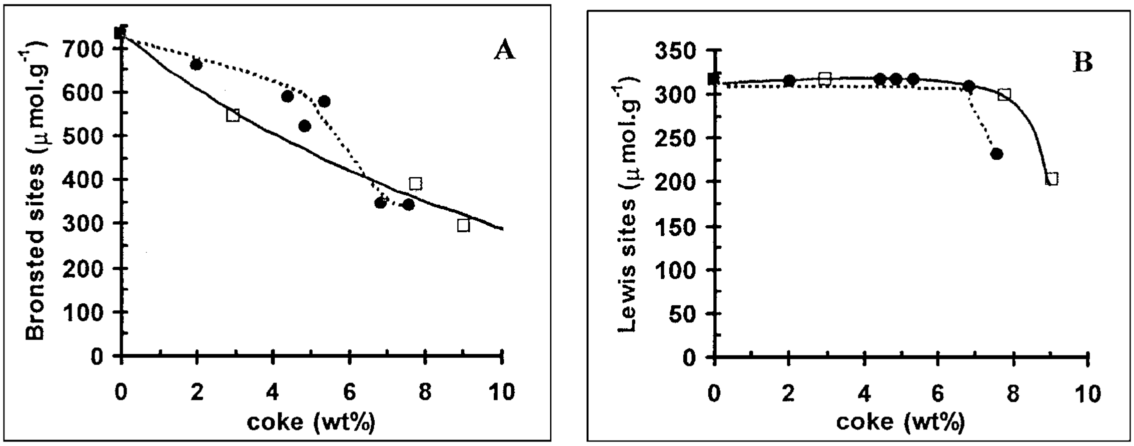


FIG. 9. Concentration of Brønsted acid sites (A) and Lewis acid sites (B) adsorbing pyridine at 423 K vs coke content. (●) 523 and (□) 723 K.

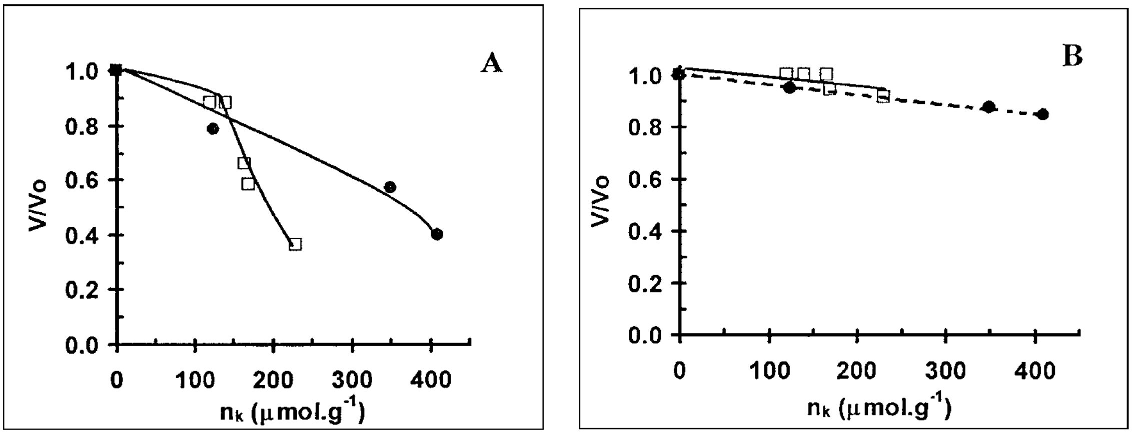


FIG. 10. Residual ultramicropore (<0.8 nm) volume (A) and supermicropore (0.8–2 nm) plus mesopore (>2 nm) volumes (B) accessible to nitrogen vs n_k, the number of coke molecules, at (●) 523 and (□) 723 K. Vo, fresh sample; V, coked samples.

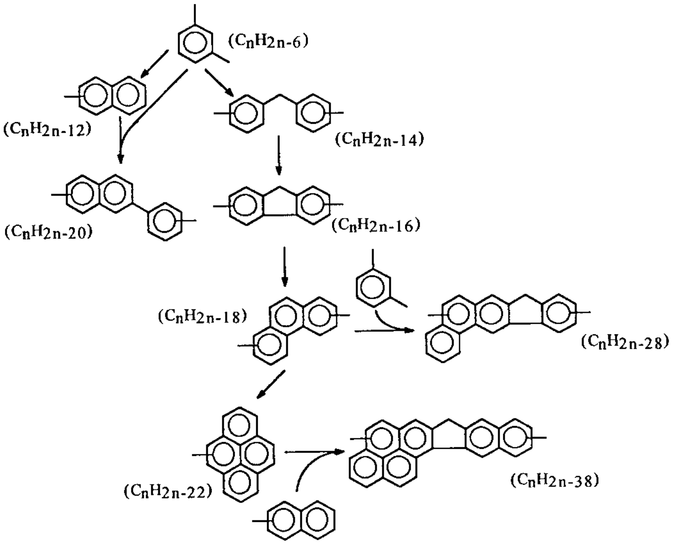
same range of coke contents. Furthermore, Fig. 10B shows that, at least for coke contents lower than 6.5 wt%, coke has no effect on the number of Lewis sites able to retain pyridine adsorbed at 423 K. Above this value, a significant decrease is observed.

DISCUSSION

Deactivation of USHY which occurs during *m*-xylene transformation at 523 and 723 K is due to the formation of carbonaceous compounds inside the zeolite pores (coke). Proposals will be made to explain the large differences observed in the composition of coke at 523 and 723 K as well as the effect of coke on conversion, accessible pore volume, and protonic acidity.

1. *Mode of Coke Formation*

1.1. At 523 K. The following reaction scheme can be proposed to explain the formation of the coke molecules (Scheme 1).

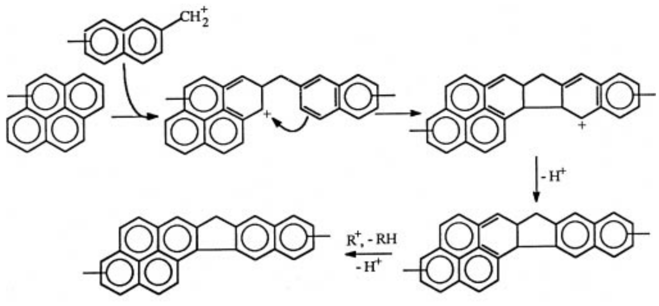


SCHEME 1

However, several families of coke components are observed as primary products (Fig. 5A), which suggests large differences in reaction rates.

The apparent primary coke molecules found at 523 K (Fig. 5A) were previously observed in the coke formed during toluene transformation over a USHY zeolite (10) and during *o*-xylene transformation over HMOR (11). Mechanisms involving diarylmethane derivatives (which are disproportionation intermediates) were proposed to explain their formation.

The secondary components (Fig. 5B) result from the same type of reactions: condensation with *m*-xylene or primary coke molecules followed by cyclization, isomerization, and hydrogen transfer steps, e.g. (Scheme 2):



SCHEME 2

At this reaction temperature, the retention of the coke molecules is not due to their steric blockage; indeed their kinetic diameter is generally smaller than the size of pore apertures. Their high boiling point, compared to reaction temperature, as well as their adsorption on the acid sites is most likely responsible for their retention inside the zeolite ultramicropores (1).

1.2. At 723 K. Three families of coke components with C_nH_{2n-22}, C_nH_{2n-26}, and C_nH_{2n-32} formulas, all soluble in methylene chloride, appear as primary products. The C_nH_{2n-38} family which is also soluble in methylene chloride and insoluble coke results from their transformation (secondary products). A large part of these coke molecules results most likely from the reactions proposed for coke formation at 523 K: alkylation with formation of diarylmethane intermediates, cyclization, isomerization, hydrogen transfer. . . However, since at high conversion there is formation of light alkenes, it is most likely that these coke maker molecules (2) also participate in coke formation.

Most of the coke molecules are located inside the zeolite micropores. This is clearly the case for soluble coke molecules which cannot be recovered in methylene chloride before dissolution of the zeolite. This is also most likely the case for insoluble coke molecules which result either from the growth through condensation with reactant and desorbed products or from simple condensation of soluble coke molecules trapped in adjacent supercages. The insoluble coke molecules resulting from the growth of soluble coke molecules have their "root" inside supercages near the outer surface of the crystallites, with the other part overflowing onto this outer surface. The other insoluble coke molecules are completely located inside the zeolite micropores. The bulkiest soluble coke molecules are sterically trapped inside the supercages: their size is between the size of the supercages and that of their apertures. The C_nH_{2n-22} molecules which are not enough bulky to be sterically blocked inside the supercages are retained because of limitations in their migration due to their large size and their adsorption on the acid sites.

2. *Influence of Coke on Conversion, Pore Volume, and Acidity*

At 723 K, there is a continuous decrease in *m*-xylene conversion with coke content, whereas at 523 K the decrease is irregular, small at first and then very pronounced (Fig. 3). From extrapolation of the curves in Fig. 3, the amount of coke which leads to a complete deactivation of the USHY zeolite can be estimated to be equal to 20 wt% at 723 K and only to 8–9 wt% at 523 K. Coke deposited at 523 K has also a larger effect on the volume of the pores accessible to nitrogen. The effect of coke on supermicropores and mesopores is very limited whereas the effect on ultramicropores is significant (Fig. 7). This confirms that *m*-xylene transformation, hence coke formation, occurs essentially in the ultramicropores. By linear extrapolation of the curves in Fig. 7A, it can be considered that a total blockage of the micropores would occur for approximately 22 wt% of coke formed at 723 K and 14 wt% at 523 K. The value found at 723 K is close to the amount of coke causing a complete deactivation, suggesting that deactivation is mainly due to pore blockage. The difference is much more pronounced for coke formed at 523 K, suggesting that deactivation by site poisoning (or coverage) plays a more significant role.

Part of the difference between the effect of coke on the micropore volume at 523 and at 723 K can be related to differences in coke composition, hence in coke density. Thus, whereas the density of coke estimated from coke composition (12) is close to 1 $g \cdot cm^{-3}$ at 523 K whatever the coke content, at 723 K it passes from 1 $g \cdot cm^{-3}$ at low coke content to 2 $g \cdot cm^{-3}$ at high coke content (only insoluble coke). From these values of coke density, it is possible to estimate the volume of coke at complete pore blockage. For both temperatures, this volume corresponds to 40–50% of the ultramicropore volume. At 723 K, the ultramicropore volume occupied by coke molecules should be even lower owing to the overflowing of the insoluble coke molecules onto the outer surface of the crystallites. This overflowing should cause a significant blockage of the access of the reactant to the micropores. This blockage is shown in Fig. 10 in which the change in the micropore volume accessible to nitrogen is plotted as a function of n_k, the number of coke molecules: the effect of coke molecules insoluble in methylene chloride is much more pronounced than the effect of soluble coke molecules. For coke formed at 523 K, this effect is practically independent of the coke content, with a slight pore blockage appearing, however, at high coke content.

It is probably because of the differences in the modes of deactivation emphasized above that deactivation (hence coke content) has a large effect on the selectivity at 523 K and practically no effect at 723 K. At 523 K, a large increase in the disproportionation/isomerization ratio is observed (Fig. 1). This means that the active sites which are affected first by deactivation are the more selective in isomerization. These sites correspond to the hydroxyl groups at 3600 and 3525 cm^{-1} (Fig. 8A) which were previously shown as the most acidic ones (6, 13–15). The strongest protonic sites are therefore very selective in isomerization. As was previously suggested (16), this very high selectivity of the strong acid sites would be due to the rapid transformation into coke molecules of the diphenylmethane intermediates of disproportionation. It should be remarked that at 523 K (Fig. 8A) the effect of coke molecules on the hydroxyl bands at 3550 and 3600 cm^{-1} is initially more limited than at 723 K (Fig. 8B). This indicates that, at 523 K, practically no coke molecules are located near these not-very-strong acid sites (hence are not formed on these sites), whereas at 723 K coke molecules could be formed on these sites. This effect of temperature was quite expected. Indeed, the higher the reaction temperature, hence the faster the reaction, the lower the acid strength necessary for its catalysis (17, 18).

Another important remark is that, at both reaction temperatures, part of the strongest hydroxyl groups are not in interaction with coke molecules even at quasi-complete deactivation (Fig. 8). This suggests that, at high coke content, blockage of the access of the reactants to zeolite pores plays a role in catalyst deactivation.

At both reaction temperatures, the effect of coke on N_{H^+} the number of protonic sites able to retain pyridine adsorbed at 423 K (Fig. 9A) is similar to its effect on *m*-xylene conversion (Fig. 3). However, at 523 K, at complete deactivation of the zeolite, N_{H^+} does not seem to be equal to zero. This shows that pyridine molecules, hence probably *m*-xylene molecules, continue, like nitrogen molecules, to acceed to part of the pore volume. This indicates also that part of the protonic sites able to retain pyridine adsorbed at 423 K are unable to catalyse *m*-xylene isomerization at 523 K. This is shown more clearly in Fig. 11, in which N_{H^+} is plotted as a function of n_k, the number of coke molecules. On the other hand, at complete deactivation at 723 K, N_{H^+} is close to zero. This confirms that acid sites, too weak to catalyze *m*-xylene transformation at 523 K, are active at 723 K.

The effect of n_k on N_{H^+} is more pronounced at 723 than at 523 K (Fig. 11A). At low coke contents (low values of n_k), part of this difference can be due to the desorption of coke molecules during pyridine adsorption, this desorption being larger for coke formed at 523 than at 723 K (1). However, this explanation is not valid at high coke contents.

It should be remarked that, at both temperatures, there is a sharp increase in the effect of n_k on N_{H^+} for a certain value of n_k. Thus, at 523 K, for $n_k \leq 300\ \mu mol \cdot g^{-1}$, each coke molecule affects only 0.6 protonic sites. This value lower than 1 can be explained by the preferential adsorption of pyridine molecules on the protonic sites (compared to the less basic coke molecules). This low value is typical of a deactivation by site poisoning. For $n_k > 300\ \mu mol \cdot g^{-1}$, each

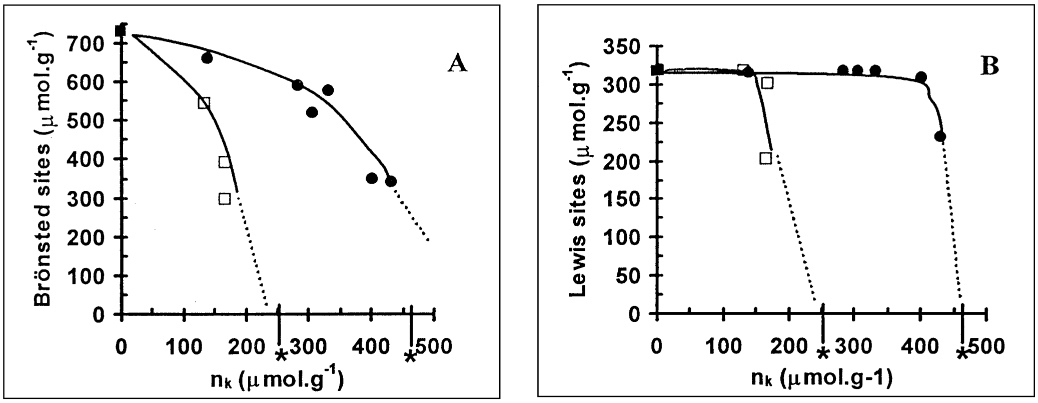


FIG. 11. Concentration of Brønsted acid sites (A) and Lewis acid sites (B) adsorbing pyridine at 423 K vs n_k, the number of coke molecules. (●) 523 and (☐) 723 K. (★) n_k at complete deactivation: 460 $\mu\text{mol} \cdot \text{g}^{-1}$ at 523 K, 250 $\mu\text{mol} \cdot \text{g}^{-1}$ at 723 K.

coke molecule causes a decrease of 2 acid sites, which indicates a limited blockage of the access to the zeolite pores. At 723 K, even at 2-min reaction ($n_k = 143\ \mu\text{mol} \cdot \text{g}^{-1}$), the $\Delta N_{H^+}/\Delta n_k$ is greater than 1 (1.3–1.4). This suggests that if deactivation occurs mainly by site poisoning, pore blockage already plays a role. Above this value, each coke molecule causes a decrease of 5 acid sites, which is quite characteristic of pore blockage.

At both temperatures and low coke contents, there is no effect of coke on N_L, the number of Lewis sites able to retain pyridine adsorbed at 423 K (Figs. 9B and 11B). This observation, already made by Vimont *et al.* (8), could indicate that Lewis acid sites are unable to catalyze coke formation. However, at high coke contents, a decrease in N_L is observed (Figs. 9B and 11B). This decrease which begins at a value of n_k higher than the value corresponding to the change in the N_{H^+} vs n_k curve (Figs. 11A) is due to a blockage by coke of the access of pyridine molecules to the Lewis acid sites.

CONCLUSIONS

During *m*-xylene transformation on a USHY zeolite at 523 and 723 K, a rapid deactivation occurs owing to a rapid formation of carbonaceous compounds inside the zeolite micropores (coke). At both temperatures, coke molecules result mainly from the transformation of diarylmethane derivatives, which are intermediates of transmethylation reactions, through cyclization, isomerization, and hydrogen transfer steps. However, at 723 K, alkylation of aromatics by alkene products followed by cyclization and hydrogen transfer steps can also play a role in coke formation. Whereas at 723 K, the retention inside the zeolite micropores of most of the coke molecules is due to their steric blockage, at 523 K it is due to their low volatility and to their adsorption on the acid sites.

At both temperatures, the number of coke molecules (n_k) was estimated for different time-on-stream values. At 523 K, n_k causes a regular decrease in the micropore volume accessible to nitrogen whereas at 723 K there is an initial slow decrease followed by a pronounced one. This pronounced decrease can be related to the blockage of the access of nitrogen to the micropores caused by highly polyaromatic molecules overflowing onto the outer surface of the crystallites. At both temperatures, coke molecules were also shown to interact first with the strongest protonic acid sites, i.e., with framework protonic sites interacting with extraframework aluminium species. The effect of n_k on the number of protonic sites N_{H^+} on which pyridine remained adsorbed at 423 K is much more pronounced for coke formed at 723 than at 523 K. However, at both temperatures, the change of N_{H^+} with n_k indicates that initially deactivation is due to site poisoning; pore blockage by coke appears at high values of n_k, the role of this mode of deactivation being always more significant at 723 than at 523 K.

No interaction of Lewis acid sites with coke molecules is observed, the only effect of coke being to block the access of reactant and adsorbate molecules to these sites. This confirms that Lewis acid sites play no direct role in *m*-xylene conversion.

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