



Prevention of zeolite deactivation by coking

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ABSTRACT

The deactivation of acid zeolite catalysts is essentially due to the formation and trapping of heavy secondary products (coke) within the pores (channels and cages). As in these nanosized pores the growth of these products is sterically limited, the coke composition, i.e., the quantitative distribution in nature and size of the components, can be determined and the scheme and mechanisms of coke formation established. Moreover, coupling activity, acidity and adsorption data with coke composition leads to information on the location and deactivating effect of coke molecules. Based on the influence on coking and deactivation rates of the features of reactions and zeolite catalysts, general rules are proposed for limiting the rate of formation of coke molecules and minimising their deactivating effect.

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1. Introduction

Owing to their shape selectivity and to the remarkable properties of their active sites, zeolite catalysts are used in many commercial processes [1–5]. These materials are largely employed as catalysts in refining (at least one zeolite-catalysed process per oil cut) and petrochemical processes: alkylation, isomerisation and transalkylation of aromatics, conversion of methanol into light olefins (MTO), etc. (Fig. 1a and b). Moreover, zeolite catalysts also play a significant role in the production of commodity and fine chemicals (Fig. 1c), as well as in pollution abatement: elimination of NO_x, volatile organic compounds (VOCs), etc. In addition, they are used in adsorption processes [2], e.g. for separating high octane number isoalkanes from *n*-isoalkane mixtures and *p*-xylene, which is an intermediate for the production of polyethylene terephthalate (PET) fibres, resins and films—from the C₈ aromatic cut, etc.

In most of these transformation and separation processes, there is a progressive decrease of the zeolite efficiency. This deactivation is mainly due to the trapping within the micropores of heavy organic compounds (called coke), which result from secondary reactions or from the deposition of feed impurities on the outer surface [6–8]. Firstly, coke can poison the active sites or block the access to them by reactant molecules. Secondly, the catalyst regeneration by coke removal requires an oxidative treatment at high temperatures with often detrimental effects, such as dealumination

and degradation of the zeolite framework, sintering of supported metals, etc.

Just as Sun Tzu sustained in his “The art of war” that knowing our enemies is crucial for success, namely the main features of their army, such as composition, location and modes of action, the same approach has to be followed for preventing deactivation by coking: it is essential to know the main features of coke, such as composition, mode of formation, location, as well as how coke affects the catalytic properties (modes of deactivation). Fig. 2 shows that, by associating to the knowledge of composition, data originated from adsorption and activity measurements, the location of coke and the modes of coking and deactivation can be determined.

2. Main features of zeolite coke

2.1. Methods for coke characterization

A large variety of analytical techniques were developed for the characterisation of catalytic coke. Their application to zeolite coke was recently described in an excellent review paper [9]. Generally, a multitechnique approach is the prerequisite to understand the modes of coking and deactivation. However, even by coupling judiciously chosen techniques, coke composition, which is the determining information (Fig. 2) is often difficult to be established. Indeed, most of the techniques generally employed lead only to information on:

- The elemental composition: e.g. H/C ratio estimated by elemental analysis of zeolite samples coked during hydrocarbon transformations or

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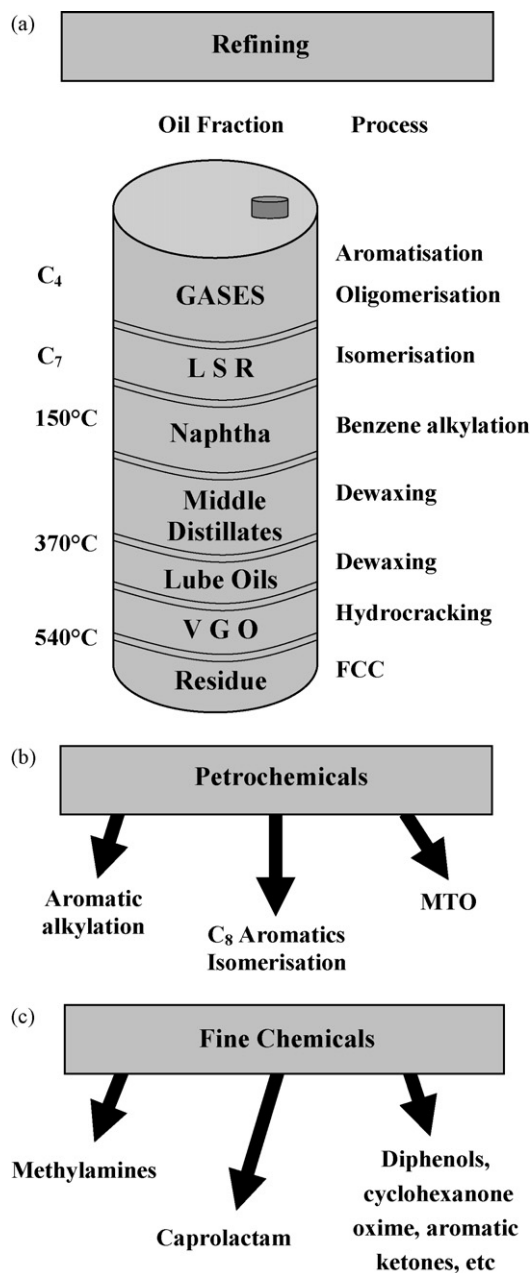


Fig. 1. Zeolite-catalysed processes in oil refining (a), petrochemicals (b), commodities and fine chemicals (c).

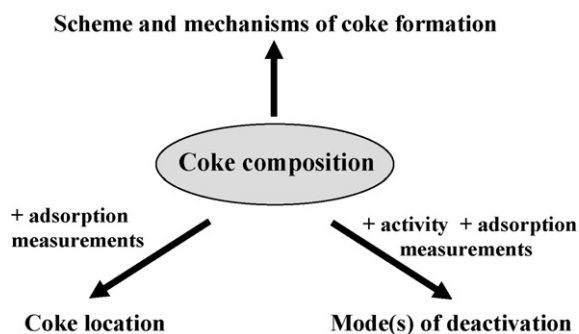


Fig. 2. Key role of coke composition for determining the modes of coke formation, the location of coke molecules and the modes of zeolite deactivation.

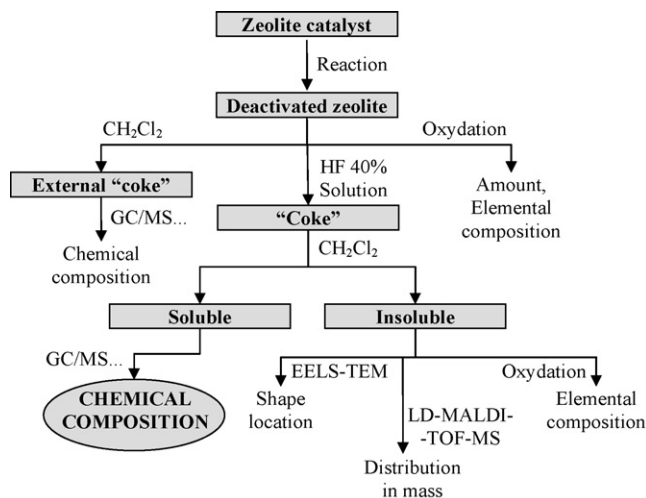


Fig. 3. Method used for determining the composition of zeolite coke. EELS: electron energy loss spectroscopy; TEM: transmission electron microscopy; LD-MALDI-TOF-MS: matrix-assisted laser desorption/ionisation/time-of-flight mass spectrometry.

– the chemical nature of the main coke components determined by spectroscopic techniques: IR, Raman, UV–vis, ¹H and ¹³C NMR, ESR, etc.; it should be underscored that these techniques present significant advantages: (a) they are non-destructive, hence several of them can be successively used; (b) operando systems, i.e., systems in which the catalytic reaction and coke characterisation are simultaneously analysed, can be developed; (c) some of them, such as IR and Raman can also specify the interaction between coke molecules and active sites (e.g. acidic hydroxyl groups).

2.1.1. Determination of coke composition

The only way to determine the coke composition, i.e., the distribution in nature and size of the components, is to separate the carbonaceous compounds from the zeolite catalyst and to analyse them by appropriate techniques. The method developed and extensively used by Guisnet and co-workers [7,10–17] is presented in Fig. 3. The first step consists of treating the coked zeolite sample with dichloromethane (CH₂Cl₂) under reflux for a long time (≥6 h), which removes soluble coke retained on the outer surface; only a small part of coke (generally less than 5%) can be recovered, which suggests that most coke molecules are trapped (and most likely formed) within the zeolite micropores. Then, the carbonaceous compounds are liberated from the zeolite by dissolution of the aluminosilicate matrix in a hydrofluoric acid solution (40%) at room temperature. Subsequently, the soluble components are extracted by CH₂Cl₂ as a solvent; in certain cases, a part of the carbonaceous compounds is insoluble and the corresponding black particles ("insoluble coke") are recovered.

The distribution of coke between soluble and insoluble fractions depends on various parameters, in particular on the reaction conditions: temperature, time-on-stream (TOS) or duration (flow or batch reactors), hence zeolite coke content, chemical nature of the reactants and on the zeolite architecture [12,14–17]. Typical examples of the effect of these parameters are given in Fig. 4 and Table 1 for reactions carried out in fixed bed reactors.

Fig. 4a shows, in the example of *n*-heptane cracking at 450 °C over a H-USY zeolite, the effect of coke content and TOS on the distribution of coke between soluble and insoluble parts: at short TOS values (hence low coke content), all the carbonaceous compounds are soluble in CH₂Cl₂; insoluble coke appears at long TOS values (hence high coke content), at the expense of soluble coke. This behaviour, which can be observed with most zeolites, shows a

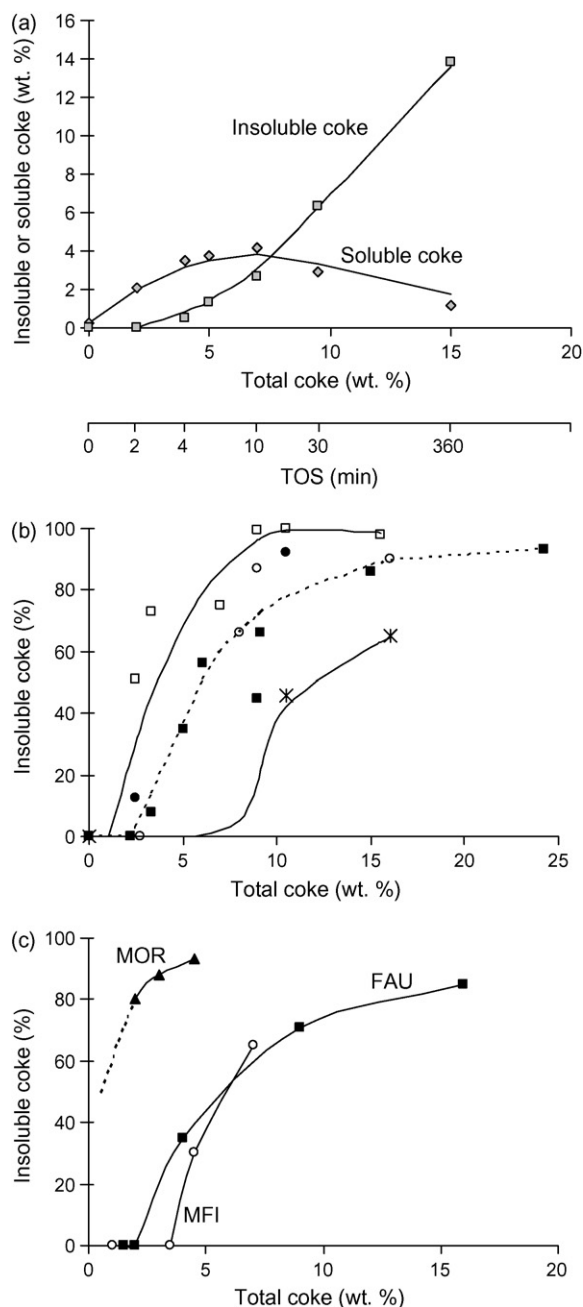


Fig. 4. Distribution of coke between soluble and insoluble parts: (a) percentage of soluble and insoluble coke formed at 450 °C on a USHY zeolite during *n*-heptane cracking vs. total coke content; percentage of insoluble coke in the carbonaceous compounds formed at 450 °C on a USHY zeolite (b) from several reactants: (○) *m*-xylene, (□) methylcyclohexane, (■) propene, (●) *n*-heptane, (*) 1-methylnaphthalene; (c) from *n*-heptane over different zeolites.

Table 1

Toluene transformation over a USHY zeolite. Influence of temperature on the characteristics of coke.

T (°C)	TOS (h)	Wt% C	Atom. H/C	Insoluble (wt%)
120	6	0.9	1.1	0
200	6	1.6	1.1	0
350	6	8.2	0.8	0
450	6	14	0.5	90
	0.25	3	0.75	45

TOS: time-on-stream.

consecutive mode of coke formation [14]:

Organicreactants → → → solublecoke → insolublecoke

The effect of temperature is generally very pronounced [12,14–17]. Typically, no insoluble coke appears at temperatures lower than 300 °C, even at high coke content, as shown with various olefinic and aromatic reactants. Thus, on a HMFI zeolite, the amount of coke formed from propene for a TOS of 5 min under similar flow conditions was equal to ~10 and 0.3 wt% at 120 and 450 °C, respectively, and despite the much higher coke content at 120 °C, all the carbonaceous compounds were soluble in CH₂Cl₂, which was not the case at 450 °C [16]. This large effect of temperature on the solubility of coke, hence on its composition (e.g. H/C ratio) is also shown in Table 1 for toluene transformation over a USHY zeolite [18].

The effect of the type of reactant and of the type of zeolite is shown in Fig. 4b and c, in which the selectivity into insoluble coke is plotted vs. the coke content. For the same amount of coke formed at 450 °C over a USHY zeolite, the selectivity to insoluble coke decreases as follows: methylcyclohexane > propene, *m*-xylene and *n*-heptane > 1-methylnaphthalene [19]. The same type of plot is used in Fig. 4c to show the effect of the zeolite pore system on the composition of coke formed during *n*-heptane cracking at 450 °C. On HMOR, a one-dimensional large pore zeolite, the main part of coke is insoluble even at low coke contents, whereas with the three-dimensional medium (MFI) and large pore (FAU) zeolites, insoluble coke appears only at high coke contents [11].

2.1.2. Limitations in the determination of coke composition

The quantitative composition of the soluble part of coke can be easily obtained through classical organic analysis techniques. Indeed, the chemical identity of the components can be determined using IR, UV-vis, ¹H and ¹³C NMR, etc. while their developed formula and their amount can be established from GC, MS and GC/MS experiments.

In contrast, it is generally impossible to establish the composition of the insoluble fraction, which consists of highly polyaromatic species. Very often, the characterisation is limited to the elemental composition. However, the recent application to insoluble coke characterisation of the matrix-assisted laser desorption/ionisation-time-of-flight mass spectrometry (MALDI-TOF MS) technique, which is successfully applied for polymer analysis, seems very promising [20–22]. This technique uses a laser beam as energy source for desorbing and ionising sample molecules, which are subsequently analysed by the time-of-flight mass spectrometer. The advantage of this technique is the relatively low input power absorbed with the consequent minimisation of fragmentation processes. Therefore, the resulting mass spectrum directly represents the molecular weight distribution of the analysed mixture. The analysis can also be carried out in the absence of a matrix (LDI-TOF MS technique).

Other physical techniques, e.g. transmission electron microscopy (TEM) coupled with electron energy loss spectroscopy (EELS), have also led to important information on insoluble zeolite coke [23,24]. For example, it was shown that the structure of coke formed during *n*-heptane cracking at 450 °C over HMFI and H-OFF zeolites was close to that of coronene (i.e., pregraphitic), while with HUSY it was more similar to pentacene (linear polyaromatic). In addition, TEM analysis showed that insoluble coke formed an envelope around the MFI crystals and appeared in filaments protruding from the HUSY micropores.

Regrettably, the techniques used for insoluble coke analysis are not very practical and, moreover, in contrast to those used for soluble coke analysis, they give only incomplete information on

composition. Fortunately, with the noticeable exception of FCC, the operating conditions (particularly the temperature) of most industrial processes using zeolites are such that a large part of coke is soluble, thus its composition can be established. Furthermore, even in the case of FCC catalysts, coke is soluble at very short TOS, hence its composition can also be determined; this information is particularly useful, since insoluble coke is essentially the result of the transformation of this soluble coke.

Therefore, it could seem surprising that most of the research groups focusing on zeolite deactivation prefer to continue to use less efficient and more costly methods for coke characterisation. The probable reason for this choice is that, in addition to be destructive, the method for coke recovery from the deactivated zeolite is somewhat laborious and, moreover, uses HF and CH₂Cl₂ which, as many chemicals, are hazardous, thus requiring serious precautions in their manipulation.

Another point to be underlined is that the application of this method is essentially limited to microporous catalysts. The reason for such a restriction is that, with classical catalysts, the majority of carbonaceous compounds responsible for deactivation are very bulky and insoluble in organic solvents, hence difficult to be characterised. As it is suggested in the first paragraph of Section 2.1.1, carbonaceous compounds responsible for zeolite deactivation are formed and trapped within the micropores. Therefore, owing to the nanosize of channels, cages and channel intersections, their growth is strongly limited by steric constraints, their molecular size and degree of aromaticity remain relatively small and the recovery of these compounds in organic solvents and their quantitative analysis are generally very easy.

2.2. From composition to scheme of coke formation

The modes of coke formation can be easily deduced from the change in coke composition with TOS (flow reactor) or duration (batch reactor), hence with coke content. Only one example will be presented here. For further information, a review paper from Guisnet and Magnoux [7] is recommended, in which a series of examples are reported, corresponding to reactions carried out over acid or bifunctional noble metal–acid catalysts either at low temperatures (<200 °C) or high temperatures (≥350 °C). A simplified scheme of coke formation from hydrocarbon reactant(s) drawn from this paper is presented in Fig. 5. In addition to the type of steps involved in coke formation, this figure shows that coke molecules can directly result from unsaturated species: alkenes, dienes, aro-

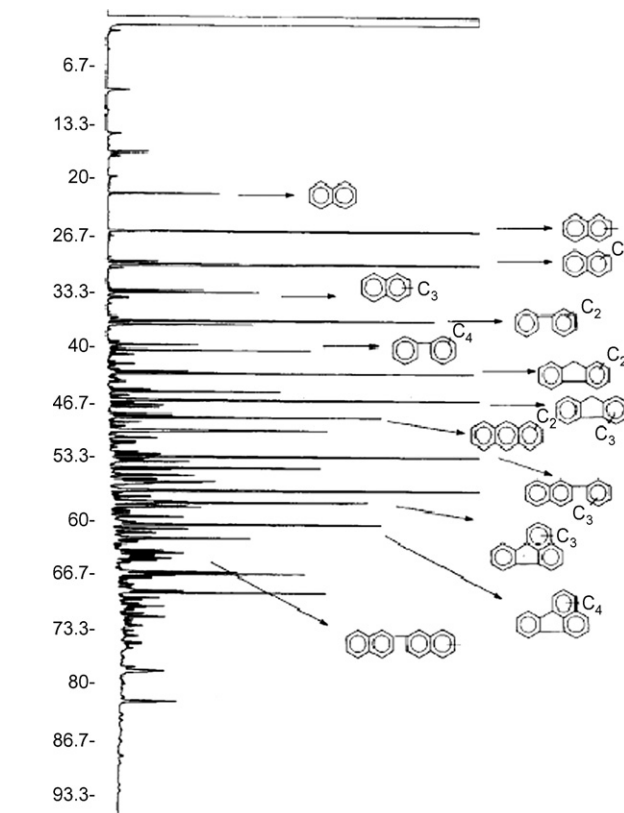


Fig. 6. Gas chromatograms of the carbonaceous compounds formed after 7.5 h (6.5 wt% coke) during *n*-butene isomerisation at 350 °C over a HFER zeolite.

omatics, etc. (primary coking) but not from alkanes and naphthenes (secondary coking).

The chosen example deals with carbonaceous deposits formed during the skeletal isomerisation at 350 °C of *n*-butenes over a HFER zeolite [25], i.e., a remarkably active and selective catalyst developed by Shell for commercial application. The method described in Fig. 3 was used to determine the composition of coke for three values of TOS, 0.5, 7.5 and 20 h, which corresponds to coke contents of 1.8, 6.5 and 7.5 wt%, respectively. In every case, all the components were soluble in CH₂Cl₂. The chromatogram of the mixture obtained for the highest coke content (Fig. 6) shows that coke contains many

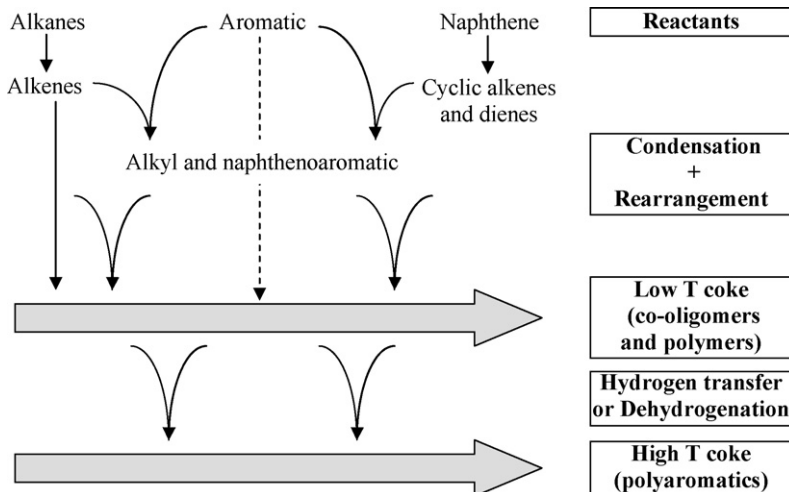


Fig. 5. Simplified scheme of coke formation from hydrocarbons over acid zeolite catalysts.

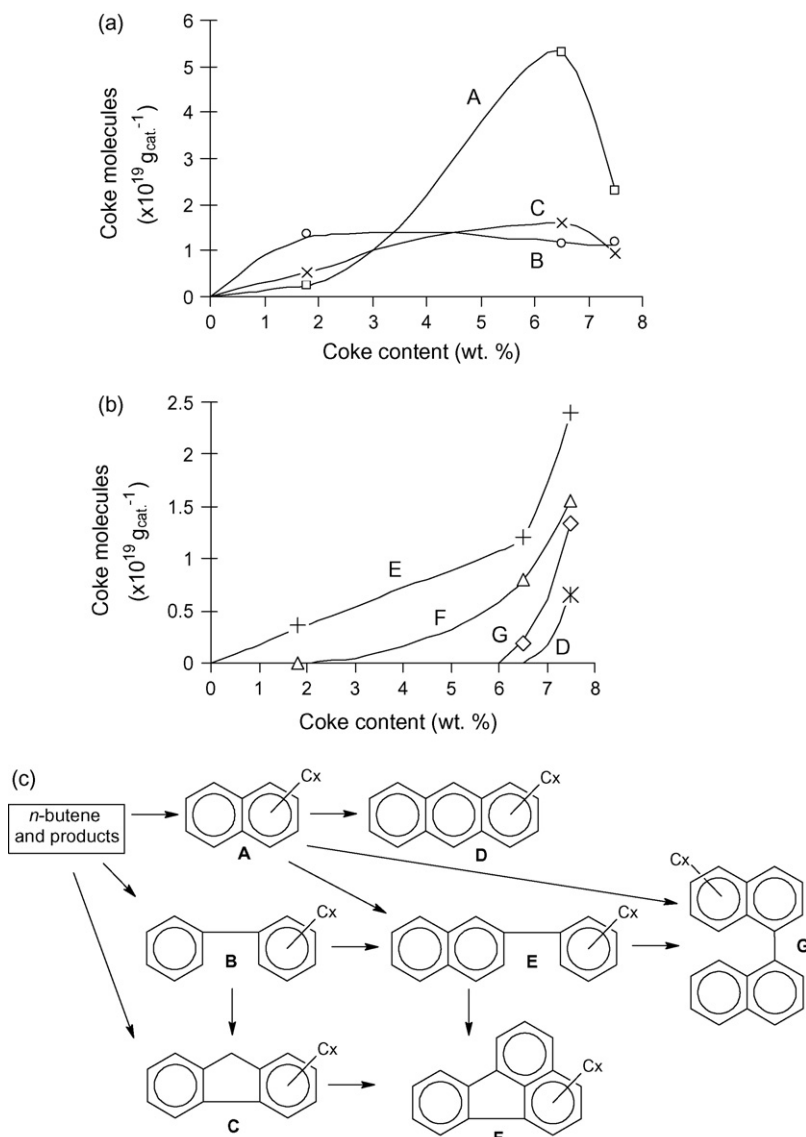


Fig. 7. *n*-Butene isomerisation at 350 °C over a HFER zeolite: (a and b) influence of coke content on the concentration of coke molecules of the various families; (c) scheme of coke formation there derived.

components. However, all of them could be identified by GC/MS as methyl-substituted (1–5 groups) polyaromatic compounds corresponding to seven families (Fig. 7). The distribution of coke in the seven families was estimated by assuming that the area of the chromatographic peaks was proportional to the amount (wt%) of the corresponding compounds (no calibration). Fig. 7a and b shows that compounds of families A, B, C and E are formed from the low coke contents while the other families appear at high contents only. Furthermore, the maximum observed in the amounts of A, B and C families suggests their transformation into other coke families. From the nature of the coke molecules and the change in their number as a function of coke content, the scheme in Fig. 7c can be proposed for explaining coke formation. It should be noted that, contrary to what can be observed with other zeolites, dehydrogenative coupling of aromatics plays an important role, in particular in the formation of compounds of the B, E and G families.

2.3. From coke composition to coke location

Two examples are presented, the first one concerning the location of coke components in the micropores of a zeolite with a double

pore system (H-OFF) [26,27] and the second discussing the possibility of direct formation of the bulky insoluble coke molecules on the outer surface of zeolite crystals. For both examples, coke was formed during *n*-heptane cracking at 450 °C.

H-OFF presents two types of micropores, both accessible by the *n*-heptane reactant: 12-MR rectilinear cylindrical channels ($6.7 \times 6.8 \text{ \AA}^2$) interconnecting through gmelinite cages with 8-MR apertures ($3.6 \times 4.9 \text{ \AA}^2$). The composition of coke was determined as a function of TOS, hence of coke content. At low contents ($\leq 0.8 \text{ wt\%}$), the carbonaceous compounds retained on the zeolite were shown to be constituted of small molecules: isobutene, mono- and bi-aromatics. Molecular modelling shows that owing to their small size, these compounds can easily desorb from the large channels, hence can only be retained in the gmelinite cages (Fig. 8a). At coke contents between 1 and 2.5 wt%, tri- and tetra-aromatic compounds appear at the expense of mono- and bi-aromatics. The comparison of their size with that of gmelinite cages suggests that these molecules, entrapped in the gmelinite cages, overflow into the large channels (Fig. 8a). Lastly, at higher contents, insoluble coke molecules, i.e., highly polyaromatic compounds, can be observed; these compounds were proposed to result from the growth of the

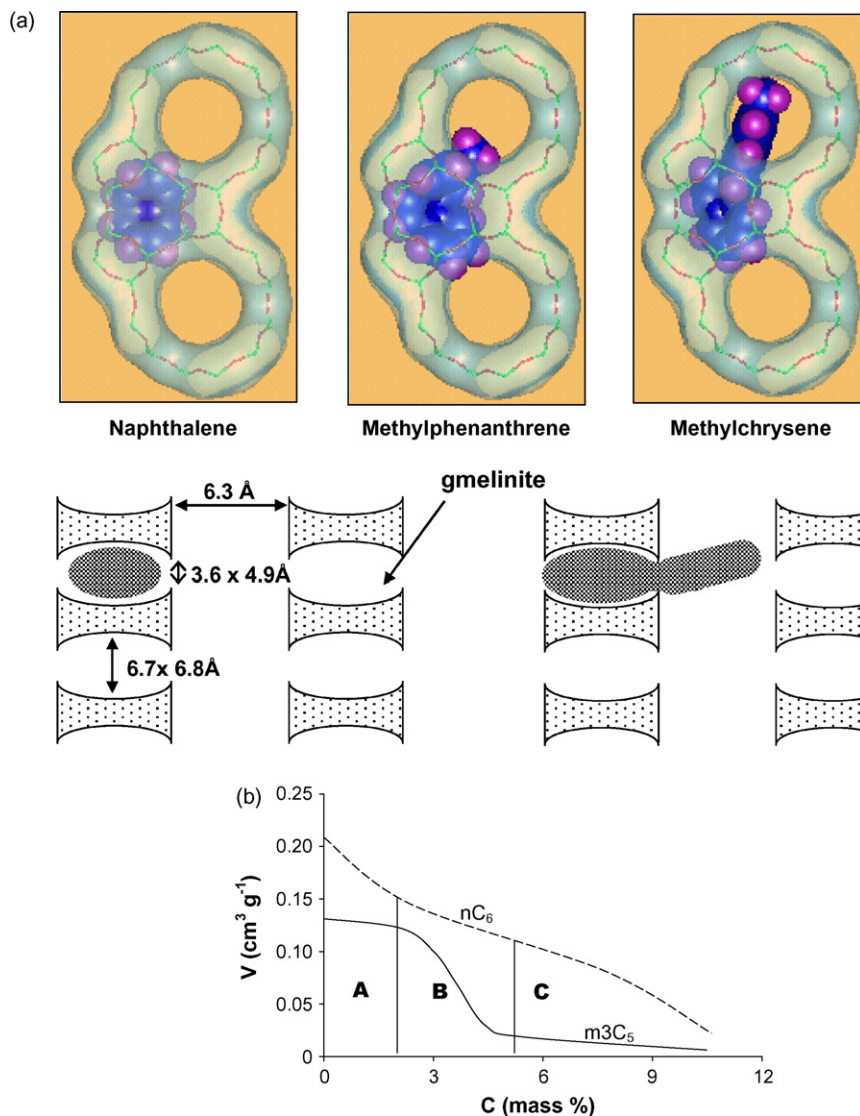


Fig. 8. n -Heptane cracking at 450°C over a H-OFF zeolite: (a) nature and location of coke molecules formed at low coke contents; (b) effect of coke content on the pore volume V accessible by n -hexane (dotted line) and 3-methylpentane (solid line) adsorbates.

coke molecules formed at lower contents with overflowing onto the outer crystal surface.

This location of coke molecules was confirmed by adsorption at 0°C of adsorbates with different molecular sizes [27]: n -hexane ($n\text{C}_6$), a molecule with a kinetic diameter similar to that of the n -heptane reactant which can enter both gmelinite cages and large channels and 3-methylpentane (3MeC_5), which can only enter the large channels. The effect of coke content on V , the volume accessible by these adsorbates, is plotted in Fig. 8b. Initially, there is a significant decrease in $V_{n\text{C}_6}$ (i.e., large channels + gmelinite cages) but no decrease in $V_{3\text{MeC}_5}$ (large channels), in agreement with the trapping of coke molecules within the gmelinite cages. For coke contents above 1 wt%, $V_{3\text{MeC}_5}$ begins to decrease in agreement with overflowing of coke molecules into the large channels. For a coke content of about 5 wt%, $V_{3\text{MeC}_5}$ becomes very small; in contrast, $V_{n\text{C}_6}$ decreases ($\sim 50\%$ of the value found for the fresh H-OFF) but remains larger than the gmelinite volume, which shows that the smaller n -hexane molecules continue to penetrate a fraction of the large channels and gmelinite cages. Above 8 wt%, $V_{n\text{C}_6}$ decreases sharply, becoming close to zero for 10 wt%, which results

from the blockage of the pore access by the heavy polyaromatic compounds overflowing onto the outer surface of the crystallites.

As indicated in Section 2.1.1, during n -heptane cracking at 450°C over various zeolites, insoluble coke molecules generally appear at the expense of soluble coke molecules, in agreement with a consecutive mode of formation. Moreover, TEM analysis of the coked zeolite samples suggests an overflowing of the insoluble coke molecules onto the outer surface of the zeolite crystals, their root being located within micropores close to the outer surface [23]. However, in certain cases, insoluble coke molecules do not result from the progressive growth of soluble coke molecules but rather from their dehydrogenative coupling. This coupling plays a major role in the case of the MCM-22 zeolite, probably because of the small distance (0.32 nm) between the supercages [28]. Therefore, the main part of the insoluble coke molecules is located in adjacent supercages (Fig. 9).

However, it is most likely that in processes operating at high temperatures and/or with heavy feeds, insoluble coke molecules can be totally retained and located on the outer surface of the zeolite

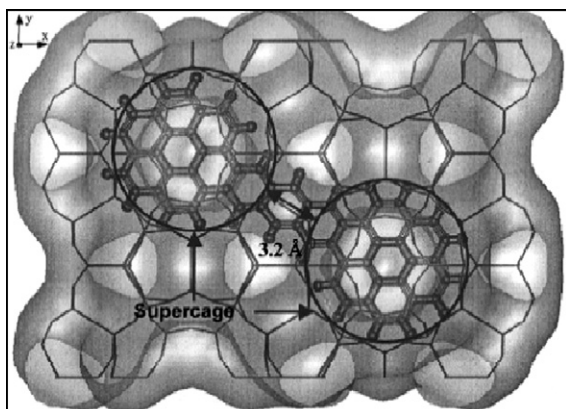


Fig. 9. Location of insoluble coke molecules formed by dehydrogenative coupling of two coronene molecules located in adjacent supercages of a MCM-22 zeolite.

crystals only. The following scheme can be suggested: formation of heavy coke precursors, migration of these precursor molecules along the catalytic bed with progressive growth up to the formation of molecules heavy enough to remain blocked (coke) on the zeolite outer surface.

3. Parameters determining the rate of coke formation

The formation of carbonaceous compounds is primarily a chemical process: coke is a stable reaction product under the operating conditions. Generally, this process is very complex, involving many successive steps (Fig. 10). Among these steps, the intramolecular (cyclisation) and intermolecular condensation reactions of reactants and/or products play a key role. These reactions, which are exothermic, are often reversible under the operating conditions, hence the concentration of the condensation products is limited by thermodynamic equilibrium. Therefore, in the absence of the reaction mixture, they are retransformed into the compounds from which they were formed (“reversible coke”). However, these condensation products undergo generally almost irreversible secondary reactions. Thus, coke molecules formed during the catalytic transformation of hydrocarbons are often very stable polyaromatic compounds, which in addition to condensation reactions, require for their formation dehydrogenation or hydrogen transfer reactions [17].

Another essential particularity of coke products is the requirement to be non-desorbed, which means that the formation of coke

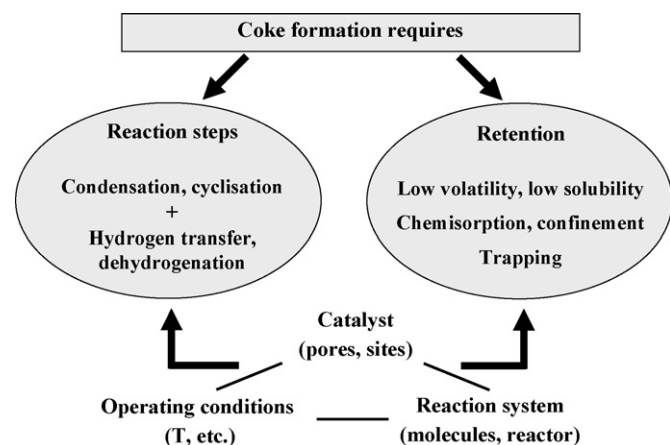


Fig. 10. Conditions required for the formation of coke over catalysts.

molecules requires not only chemical steps, but also their retention within the pores or on the outer surface of the catalyst [17]. The retention of coke molecules within the pores may be due (i) to their steric blockage (trapping), (ii) to their strong chemisorption on active sites and their confinement within the pores and (iii) to their low volatility (gas phase reaction) or solubility (liquid phase reaction) (Fig. 10). These three possibilities can occur independently or in association. Furthermore, the retention on the outer surface is usually due to the low volatility (or solubility) of coke molecules.

In both aspects of coke formation – chemical process and retention – the characteristics of the catalyst-reaction couple play a decisive role (Fig. 10). Thus, the composition, location of coke and rate of formation are determined by:

- The features of the reaction: type and rate of the desired and secondary transformations that reactants may undergo, size and shape of reactant and product molecules, characteristics of the reactor.
- The operating conditions (T , pressure, etc.).
- The features of the catalyst: nature, number, strength and location of the active sites, size and shape of pores and openings.

3.1. Influence of the reaction system

On acid catalysts, coking occurs rapidly from certain molecules which can be considered as coke precursors or coke maker molecules [15,17,29]. Alkenes, dienes and polyaromatics are typical coke maker hydrocarbons. Coke maker molecules should satisfy the following conditions: either to be highly reactive and/or to be strongly retained on the outer surface or within the zeolite micropores.

- Thus, short chain alkenes and dienes (especially cyclopentadienes) are highly reactive in acid catalysis. On acid zeolites, these molecules undergo very fast condensation reactions (oligomerisation, polymerisation), leading to heavy and polar products which can be easily retained on the zeolite. Moreover, these products are reactive enough to undergo monomolecular reactions, such as cyclisation, and also bimolecular reactions, such as hydrogen transfer, leading then to coke molecules.
- Polyaromatic molecules are less reactive than short chain alkenes but because of their bulkiness and their polarity (basicity), these heavy compounds are strongly retained on acid zeolites. Therefore, their contact time with the acid sites is very long, which favours their transformation into heavier molecules that cannot desorb from the zeolite, i.e., can be considered as coke molecules.

It can be noted that, as was underlined in Fig. 10, both conditions of reactivity and retention always have to be satisfied, the first one playing the determining role in coke formation from light alkenes and from dienes, the second in coke formation from polyaromatics.

Coke formation occurs slowly from non-substituted monoaromatics, from alkanes and naphthenes whose transformation into alkenes and polyaromatics is slow. In this case, the formation of these coke maker molecules becomes the determining step of coking. Unfortunately, coke maker molecules are often intermediates or products of the desired transformation of these poorly reactive compounds. A typical example is the isomerisation of n -alkanes, in which acid zeolite catalysts are generally rapidly deactivated by coke resulting of alkenes and dienes present (even in low amounts) in the reaction mixture. The solution to limit coke formation, hence deactivation, is to decrease the concentration of these coke precursor molecules, for instance by operating under hydrogen pressure over bifunctional catalysts, such as Pt/mordenite. Under

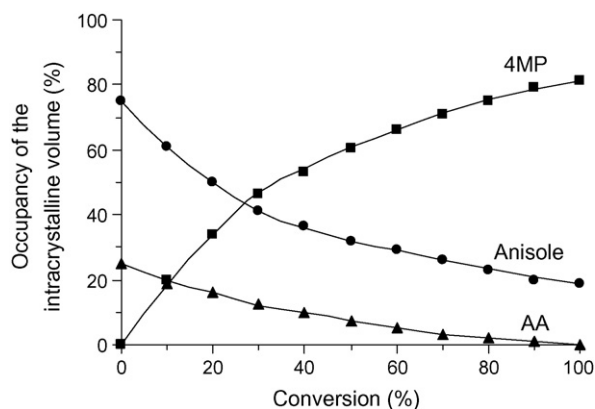
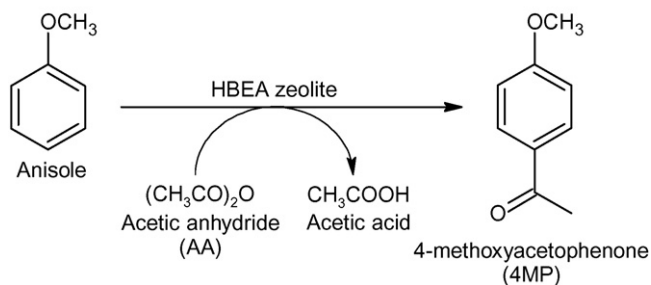


Fig. 11. Transformation in a batch reactor of a 2:1 molar anisole:acetic anhydride mixture over a HBEA zeolite: relative occupancy of the intracrystalline volume by anisole (●), acetic anhydride (▲) and 4-methoxyacetophenone (■).

these conditions, olefinic intermediates of the bifunctional process are formed in trace amounts, sufficient to allow bifunctional isomerisation, but not enough to undergo the bimolecular reactions involved in coke formation.

Another way to limit coke formation is to favour desorption of coke precursors, in order to prevent their transformation. This method is currently used when coke precursors are the desired products, as it is often the case in the liquid phase synthesis of fine chemicals [8]. Indeed, in these reactions, the product molecules are generally bulkier and more polar than the reactant molecules. As a consequence, the reactions are limited by product desorption, not only from the active acid sites, but also from the zeolite micropores. This was nicely demonstrated by Derouane et al. [30] in the example of anisole acetylation with acetic anhydride (AA) over a HBEA zeolite.

Graphic 1



From a kinetic study, the adsorption equilibrium constants K of anisole, AA and of the desired 4-methoxyacetophenone (4MP) product were estimated and the K values were used to estimate the relative occupancy of the intracrystalline volumes by these three compounds. The K value for 4MP was found to be ca. 10 and 6 times greater than the K values of AA and anisole respectively, and as a consequence, the intracrystalline volume of HBEA was, at high conversion, preferentially occupied by 4MP (Fig. 11). This preferential occupancy strongly affects the catalyst stability for two reasons: (i) the reaction is self-inhibited and (ii) the long contact time of 4MP molecules with acid sites favours their secondary transformation into bulkier and more polar products which remain trapped within the zeolite micropores, blocking their access by reactant molecules. By operating acetylation at low conversion, using a large excess of anisole, substituting batch reactors by flow reactors, etc. the stability of the zeolite catalyst was significantly improved, allowing the development by Rhodia of an efficient commercial process [31].

3.2. Influence of reaction temperature, T

The effect of T on the rate of coking depends on the reactant [17]. With coke maker molecules as reactant, the plot representing the coking rate as a function of T passes through a minimum. This type of curve was found for coke formation during propene transformation over a HMFI zeolite (Fig. 12a). This complex behaviour can be related to the fact that the coking rate depends on the rates of chemical steps and of retention of the coke molecules and that, as it will be shown below, both the types of chemical steps and the cause of trapping depend on T .

With poorly reactive reactant molecules, such as *n*-heptane, the rate of coking increases continuously with T , in agreement with the limitation of coke formation by the formation of coke maker molecules, e.g. of alkenes by *n*-heptane cracking.

Reaction temperature has a very significant effect on the composition of coke and it is usual to classify coke into low temperature ($\leq 200^\circ\text{C}$) and high temperature ($> 350^\circ\text{C}$) cokes [7]. As an example, the large difference between these types of coke is shown in Fig. 12b for propene transformation over HMFI [32]. At 120°C , coke is constituted of diolefins, olefins and alkanes with 10–35 C atoms, the formation of which requires a series of alkylation and cracking steps plus some hydrogen transfer steps. At 450°C , coke is constituted of methylpolyaromatic compounds, such as methylpyrenes, which result from a series of alkylation, cyclisation and hydrogen transfer steps. From the comparison of the molecular size of carbonaceous compounds with the dimensions of pore apertures and of their boiling point with the reaction temperature, it is easy to deduce that, at low temperatures, coke retention results from the low volatility of the components, while at high temperatures, it results from their trapping within the micropores. Molecular modelling (Fig. 12c) confirms that methylpyrenes can effectively be accommodated and trapped at the channel intersections of the MFI zeolite. Trapping of coke molecules formed at high reaction temperatures at channel intersections or within cages was shown to be a general phenomenon [14].

3.3. Influence of the acid zeolite features

The main features of acid zeolite catalysts, on the one hand the concentration, strength and proximity of the acidic active sites (generally the protonic ones), on the other hand the size and shape of the cages, channels and channel intersections (i.e., the nanoreactors) play a major role in the various successive chemical steps involved in coke formation, as well as in the retention of precursor and coke molecules [14]. Because of the difficulty in obtaining zeolite samples with identical acidities and with different pore structures and vice versa, it is generally difficult to quantify the effect of these parameters. Having said that, some examples are given hereafter, illustrating the respective roles of acidity and of pore structure.

The following could be expected on the role of the acidity characteristics (Fig. 13): (i) the stronger the acidic sites, the faster the chemical steps and the more pronounced the retention of coke precursors and coke molecules, hence the faster the coking rate; (ii) the higher the density of the acid sites, thus the closer these sites are to each other, the larger the number of successive chemical steps undergone by reactant molecules along the diffusion path within the zeolite crystallites and the more favourable the condensation reactions, hence the faster the coking rate.

The effect of acid strength was clearly demonstrated in *n*-heptane cracking at 350°C by using as catalysts two series of dealuminated FAU (Y) samples [33]. The first one resulted from steaming of a NH_4NaY zeolite, thus contained a large amount of extra-framework aluminium species (EFAL). The second resulted

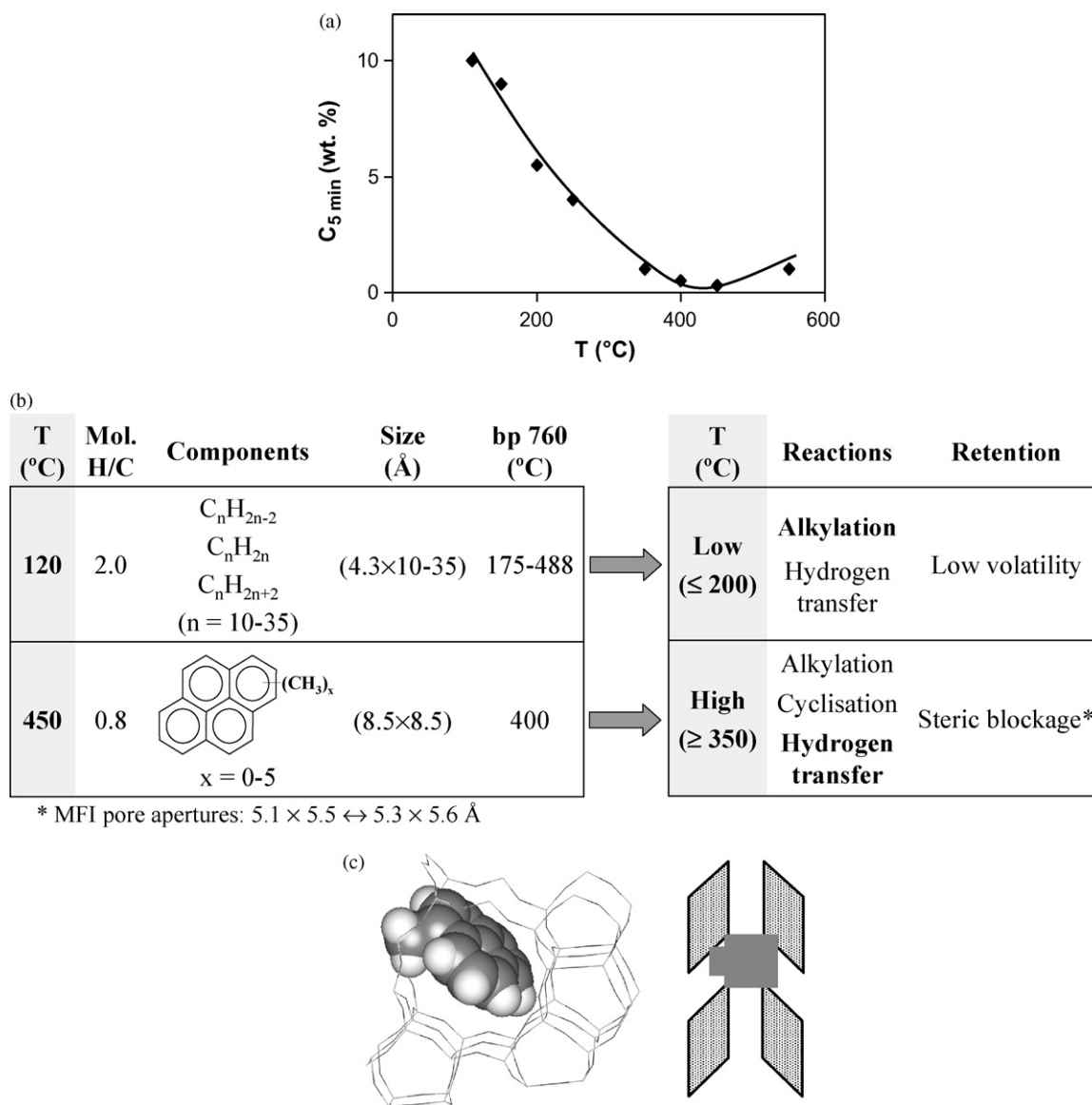


Fig. 12. Influence of temperature on the amount of coke deposited during the first 5 min of propene reaction on a HMFI zeolite (a) and on the composition of coke and the chemical and physical steps involved (b); molecular model showing a methylpyrene molecule trapped at the channel intersections of the HMFI zeolite (c).

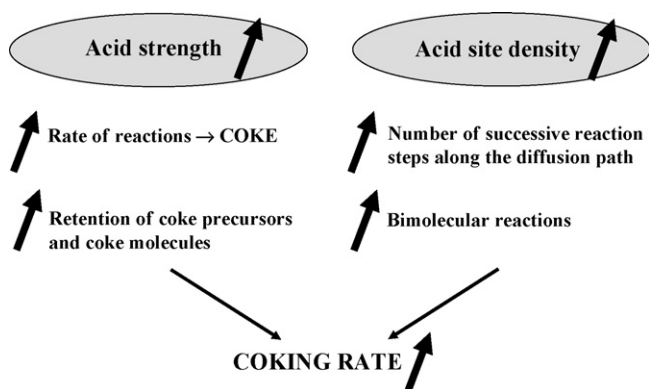


Fig. 13. Influence of the characteristics of the catalyst acidity on the rate of coking.

from treatment of the samples of series 1 with a dilute HCl solution, in order to eliminate the EFAL species without modifying the zeolite framework. As coking of *n*-heptane is consecutive to cracking, the ratio between coking and cracking rates should be considered (instead of the coking rate) to discuss the effect of acidity. Fig. 14 shows that for identical values of the concentration of protonic sites per unit cell, this ratio is greater for the samples of series 1, which suggests that EFAL species have a promoting effect on the selectivity to coke. This promoting effect can be related to the well-demonstrated enhancement of the acid strength of protonic sites by their interaction with EFAL species presenting Lewis acidity. This increase of the protonic acid strength is confirmed by the presence in the IR spectrum of the series 1 samples (with EFAL species) of an additional OH band at 3600 cm⁻¹, which corresponds to very strong acid protonic sites, able to retain pyridine adsorbed at very high temperatures (>450 °C, under vacuum) [34].

The effect of pore structure was first investigated by Rollmann and Walsh [35] by comparing the transformation at 427 °C of an equimolar mixture of *n*-hexane, 3-methylpentane,

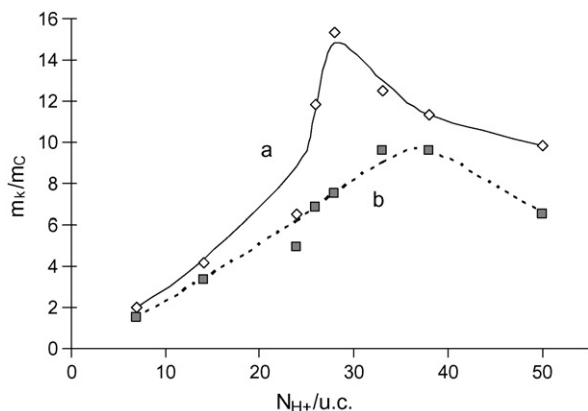


Fig. 14. Coke formation during *n*-heptane cracking at 350 °C over dealuminated HFAU (HY) zeolites. Ratio (m_k/m_c) between the amounts of coke and cracking products vs. the number of protonic sites per unit cell ($N_{H^+}/u.c.$). Curve a: samples with a large amount of extra-framework Al species; curve b: samples with a low amount.

2,3-dimethylbutane, benzene and toluene over a large series of zeolites. The size of the pore apertures was found to be the determining parameter, with selectivity to coke decreasing from 1 with large pore zeolites, to 0.1 and 0.05 with medium and small pore zeolites, respectively. This conclusion seems surprising, since it excludes an effect of the features of cages, channels and channel intersections, in which at high temperatures coke molecules are formed and sterically trapped. More recent work leads, however, to different conclusions.

The first one deals with coke formation during *n*-heptane cracking at 450 °C over four protonic zeolites with different pore structures [11,14]. The degree of protonic exchange was chosen so that initial cracking activities were similar. The initial coking/cracking rate ratio was found to be close to 1 with HMOR and HERI, 4 times lower with HFAU and 1000 times lower with HMFI. The high selectivity to coke of the first two zeolites was attributed to the fast blockage of coke precursors in the one-dimensional channels of HMOR or in the trap cages of ERI, i.e., large cages ($6.3 \text{ \AA} \times 13 \text{ \AA}$) with small apertures ($3.6 \times 5.1 \text{ \AA}^2$). These features, favourable to the formation of coke, do not exist in FAU and MFI, which have three-dimensional pore systems with smaller differences between the dimensions of cages (FAU) or channel intersections (MFI) and those of apertures: while FAU presents cages of

$13 \text{ \AA} \text{ \AA}$ and apertures of $7.4 \text{ \AA} \text{ \AA}$, MFI displays channel intersections of $\sim 8.5 \text{ \AA} \text{ \AA}$ and pore apertures of $5.3 \times 5.6 \text{ \AA}^2$ and $5.1 \times 5.5 \text{ \AA}^2$. With this latter zeolite, the smaller difference largely explains the very low coking activity. However, an additional reason could be the low acid site density of the chosen MFI sample [11,14].

The large effect of the micropore characteristics on coke formation can be shown by using the MCM-22 zeolite only. Indeed, in contrast with most other zeolites, MCM-22 presents independent pore systems [36]:

- Large cylindrical supercages ($7.1 \text{ \AA} \text{ \AA}$, 18.4 \AA height) interconnected through 10 MR windows ($4.0 \times 5.5 \text{ \AA}$).
- Two-dimensional narrow 10-MR sinusoidal channels ($4.0 \times 5.0 \text{ \AA}$) which form a small cage at their intersection ($6.4 \times 6.9 \text{ \AA}$).
- Large 12-MR cups ($7.1 \text{ \AA} \text{ \AA}$, 7 \AA depth) on the external surface of MCM-22 crystals, which corresponds to hemisupercages.

The three pore systems contain bridging OH groups, i.e., protonic acid sites and acid-catalysed reactions, such as xylene isomerisation, were shown to occur in each of them, although with differences in turnover frequency, selectivity and stability. Whatever the reaction, a rapid formation of carbonaceous products occurs within the large supercages, causing their very fast deactivation [37]. This behaviour could be expected from the large difference between the dimensions of the supercages and of their apertures: supercages can be considered as trap cages. Thus, in these large cages, xylene disproportionation, which involves bulky bimolecular intermediates, can occur in addition to isomerisation. During their slow desorption through the narrow apertures of the supercage pore system, the bulky trimethylbenzene products undergo various transformations leading to smaller products and to carbonaceous compounds.

In contrast, there is practically no deactivation of the reactions occurring within the sinusoidal channels and external cups [37,38]. Within the narrow sinusoidal channels, this can be related to the difficulty of forming “coke” precursors. The small difference between the sizes of apertures and channel intersections also makes molecular trapping unlikely. The explanation for the high stability of external cups is quite different [38]. Indeed, in these large cups, steric limitations should not affect the chemical steps involved in the formation of bulky product molecules, hence of carbonaceous compounds. However, these carbonaceous compounds cannot be observed, most likely because the second condition for

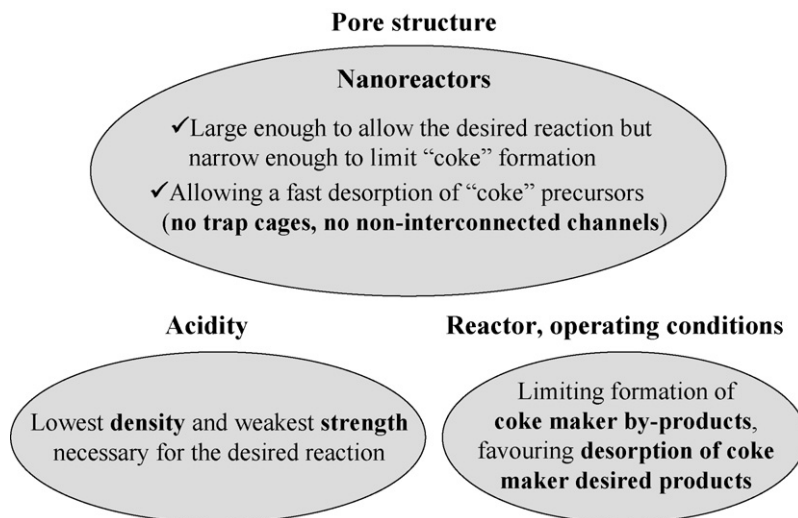


Fig. 15. Guidelines for limiting coke formation over zeolite catalysts.

coke formation, i.e., the possibility of retention of coke precursors, is not satisfied. This difficulty for retaining molecules within the outer cups can be related to their large diameter and their small depth, which favour the desorption of the primary products by sweeping, thus preventing their secondary transformation [38].

4. Guidelines for limiting the formation of coke

From the effects that the zeolite characteristics, the operating conditions and the reaction system have on the rate of coking, general rules for limiting the formation of coke can be set up. The most important are reported in Fig. 15.

5. Modes of deactivation

It is generally accepted that coke affects the activity of porous catalysts in two different ways [6]: poisoning (or coverage) of the active sites and pore blockage. In the case of site poisoning, one active site is deactivated per coke molecule. However, the deactivating effect can be more limited when reactant molecules are able to compete with coke molecules for adsorption on the active sites. Pore blockage generally causes a significant deactivation. Indeed, the access of reactant molecules to a channel or a cage, hence to all the active sites they contain, can be blocked by a single coke molecule. The partial limitation of the access of reactant molecules by coke, which has a smaller effect, is sometimes associated to this mode of deactivation.

5.1. Method for determining the mode of deactivation

As shown in Fig. 2, the modes of deactivation by coking can be determined by associating to the knowledge of coke composition, data originating from activity and adsorption measurements at different values of TOS, hence of coke content. From the amount and composition of coke, the concentration of coke molecules (C_k) can be estimated, the obtained values being accurate only when coke is totally soluble in dichloromethane.

With this concentration value, the decrease in activity can be related to coke molecules instead of coke content and the deactivating effect of the coke molecules can be established [11]. However, to determine what is sometimes called the “toxicity” (T) of coke molecules, i.e., the number of active sites deactivated per coke molecule, a relation between activity and concentration of active sites is necessary. With acid zeolites as catalysts, this can be done by determining the effect of coke on the bridging OH groups, which are generally the active sites. However, in the first studies of the mode of zeolite deactivation, it was simply supposed that all the active sites had the same activity [11]. With this assumption, T can be easily drawn from the change in the residual activity A/A_f vs. C_k/C_{Af} , the ratio between the concentrations of coke molecules and of active sites of the fresh zeolite. As an example, Fig. 16a shows the plot obtained for *n*-heptane cracking at 450 °C over a HMFI zeolite; C_{Af} , which appears in the C_k/C_{Af} in abscissa corresponds to the concentration of strong acidic sites of the fresh zeolite (determined by NH_3 adsorption), which were admitted to be the active sites in *n*-heptane cracking. In this graph, T is given by the slope of the curve. In the three domains of coke content which were considered (A, B, and C), the average value of T was equal to 0.25, 1 and ~ 3 , respectively.

Furthermore, from the concentration (C_k) and nature of coke molecules, the volume really occupied by the coke molecules (V_R) can be determined through molecular modelling. This volume can be compared with the volume apparently occupied by the coke molecules (V_A), measured by adsorption of probe molecules. Nitro-

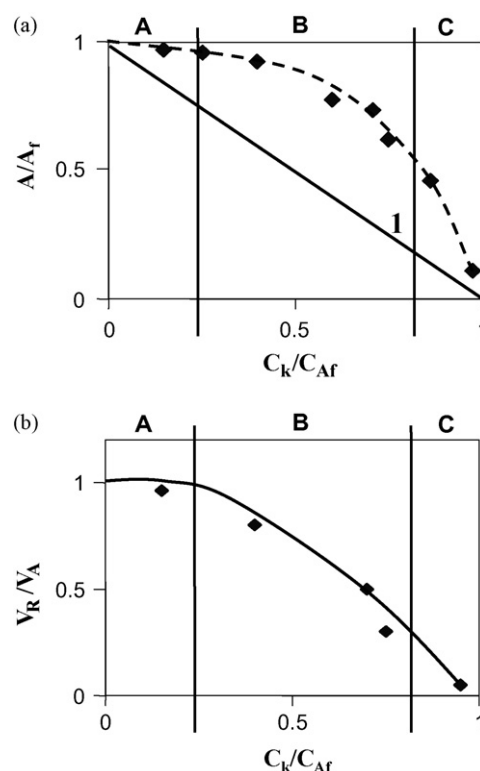


Fig. 16. *n*-Heptane cracking over a HMFI zeolite at 450 °C. Plots of the residual activity A/A_f (a) and of the ratio between the volumes apparently and really occupied by coke V_R/V_A (b) vs. C_k/C_{Af} , the ratio between the concentrations of coke molecules and of active sites of the fresh zeolite.

gen and *n*-hexane adsorption at -196 and 0 °C, respectively, were used for characterising zeolite samples coked at different TOS during *n*-heptane transformation at 450 °C. With the HMFI sample, identical values were found with both adsorbates. Fig. 16b shows that, with this zeolite, the V_R/V_A ratio decreases from 1 at low values of C_k/C_{Af} (domain A) to practically zero at high values (domain C).

From the values of T and of V_R/V_A , the modes of deactivation of the HMFI zeolite can be easily established for each of the three domains of C_k/C_{Af} [11,14]. Indeed, in domain A, the value of 1 for V_R/V_A demonstrates that there is no pore blockage, the T value lower than 1 (0.25) suggesting a competition for adsorption on the protonic sites between the reactant and the coke molecules, which are weakly basic (as shown by the coke composition). In domain B, T is equal to 1, which suggests a deactivation by site poisoning; however, V_R/V_A is lower than 1, which indicates a blockage of the access of adsorbate molecules to part of the porosity unoccupied by coke molecules. This apparent disagreement can be easily explained by considering that the coke molecules which are trapped at the channel intersections of the MFI zeolite completely block their access, without occupying the totality of their volume (Fig. 17b). In domain C, both values of $T (>1)$ and $V_R/V_A (<1)$ point to deactivation by pore blockage (Fig. 17c). In this domain, coke contains insoluble components which recover part of the crystal outer surface, providing an additional argument in favour of this mode of deactivation.

5.2. Pore structure and mode of deactivation

The same experiments were carried out over three other protonic acid zeolites with similar initial cracking activity: two

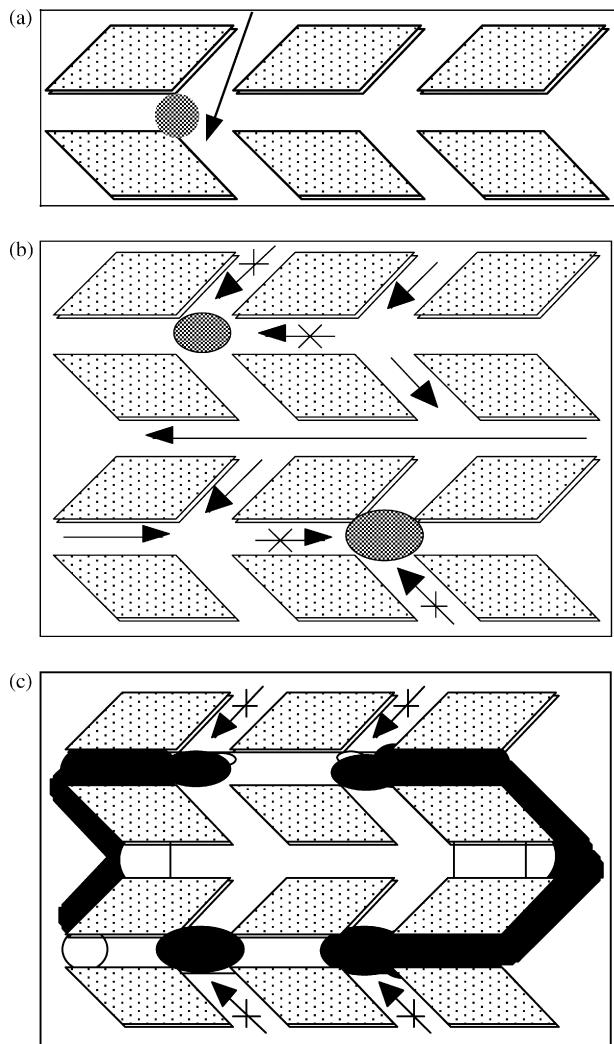


Fig. 17. *n*-Heptane cracking over a HMFZ zeolite at 450 °C. Modes of deactivation (a and b): site coverage; (c) pore blockage.

large pore zeolites, HFAU and HMOR and a small pore zeolite, HERI. Within the micropores of HFAU and HERI, both adsorbate molecules (nitrogen and *n*-hexane), as well as the *n*-heptane reactant molecules, can diffuse tridirectionally. With HMOR, *n*-hexane and *n*-heptane molecules can diffuse only along the large channels, while the smaller nitrogen molecules accede to both large and small channels.

The effect of coke molecules on the residual activity (A/A_f) and on the ratio between the micropore volumes really and apparently occupied by coke molecules (V_R/V_A) is very different with HFAU (Fig. 18a and b) and the other two zeolites (Fig. 19a and b).

With HFAU, there is initially about four active sites deactivated per coke molecule ($T \approx 4$); however, above a C_k/C_{Af} value of 0.15, T decreases, becoming close to 1 at complete deactivation (extrapolated value) (Fig. 18a). The effect of coke on the value of V_R/V_A depends on the adsorbate molecule (Fig. 18b): with nitrogen, $V_R/V_A = 1$ at low C_k/C_{Af} value and it progressively decreases for $C_k/C_{Af} > 0.15$ up to a value of 0.5; with *n*-hexane, V_R/V_A is close to 1 at very low C_k/C_{Af} values, decreasing rapidly and then more progressively up to a value of 0.4. From nitrogen adsorption, it can therefore be deduced that for $C_k/C_{Af} < 0.15$, there is no blockage of the access to the micropore volume unoccupied by coke molecules, meaning that deactivation is due to site poisoning or coverage. However,

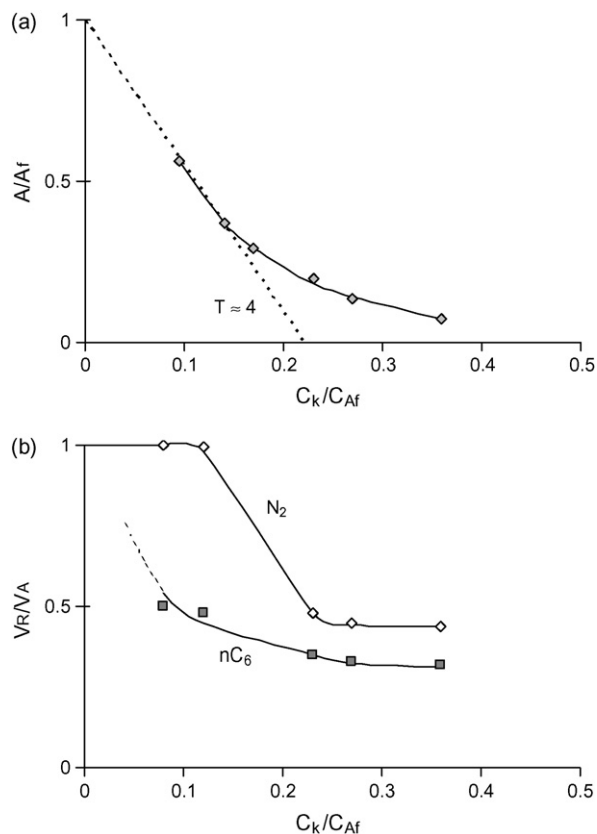


Fig. 18. *n*-Heptane cracking over a HFAU zeolite at 450 °C. Plots of the residual activity A/A_f (a) and of the ratio between the volumes apparently and really occupied by coke V_R/V_A (b) vs. C_k/C_{Af} , the ratio between the concentrations of coke molecules and of active sites of the fresh zeolite.

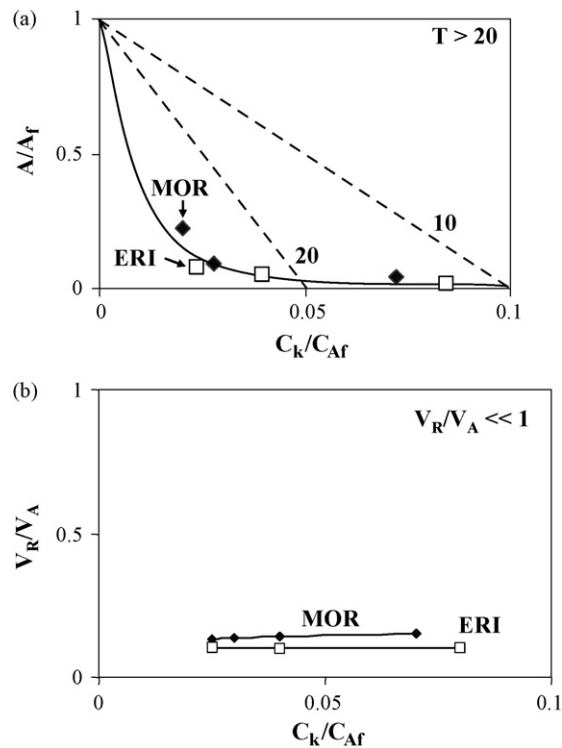


Fig. 19. *n*-Heptane cracking over HMOR and HERI zeolites at 450 °C. Plots of the residual activity A/A_f (a) and of the ratio between the volumes apparently and really occupied by coke V_R/V_A (b) vs. C_k/C_{Af} , the ratio between the concentrations of coke molecules and of active sites of the fresh zeolite.

this conclusion is only valid if it is considered that the diffusion of the *n*-hexane adsorbate within the micropores of the coked HFAU is limited by coke, whereas that of the *n*-heptane reactant is not. This is quite possible, the easier diffusion of *n*-heptane molecules being due to the much higher reaction temperature (450 °C) than the 0 °C used for adsorption experiments. Another observation to be explained is the value of T higher than 1 (~ 4), that seems in disagreement with deactivation by site poisoning. This high value can be related to the heterogeneity in acid strength of the OH groups of this zeolite, in particular to the presence on the FAU sample used in this study of very strong (hence very active) protonic sites, resulting from interaction with extra-framework Al species (cf. Section 3.3). IR characterisation confirms this proposition, showing in addition that the first coke molecules interact with the corresponding hydroxyl groups [39]. The preferential reaction of *n*-heptane (cracking and coking) on these strong sites accounts also for the decrease in T observed for $C_k/C_{Af} > 0.15$, despite the pore blockage shown by the adsorption results obtained with both *n*-hexane and nitrogen adsorbates. From the results obtained with HFAU, only modes b (classical site poisoning) and c (pore blockage), described in Fig. 17b and c, are clearly demonstrated. It is, however, most likely that, at very low coke contents, deactivation of HFAU results from mode a, as observed with HMFI.

The case of HMOR and HERI is much simpler. Indeed, very high values of T (> 20) are found for low values of C_k/C_{Af} (< 0.05), which is typical of pore blockage. This conclusion is moreover, supported by the low values of $V_R/V_A \sim 0.1$ with both zeolites (Fig. 19b). It should, however, be noted that, while with HERI these low values are found with both adsorbates (*n*-hexane and nitrogen), with HMOR the values reported in Fig. 19b correspond to *n*-hexane as adsorbate; indeed, with nitrogen, values of V_R/V_A close to 1 can be observed for low values of C_k/C_{Af} , which means that all the micropore volume unoccupied by coke is accessible by nitrogen molecules. This can be explained by the ability of the small molecules of nitrogen (kinetic diameter of 3.6 Å) to reach the free volume of the large channels by diffusion through the narrow channels. However, V_R/V_A for nitrogen decreases significantly with the increase in coke content and, for $C_k/C_{Af} \geq 0.04$, it is equal to the value found with *n*-hexane. This blockage of nitrogen access to the pore volume is probably due to insoluble coke molecules overflowing onto the crystal outer surface [11].

6. Parameters determining the deactivating effect of coke

As shown in Section 5.2, the deactivating effect of coke molecules (quantified by the T values) depends significantly on the zeolite pore structure and on the coke content:

- With three-dimensional zeolites having no trap cages (large cages with small apertures), such as MFI and FAU, deactivation that is caused at low coke contents by site poisoning progressively evolves to pore blockage with the increase in coke content. Therefore, when the acid sites have similar features, in particular similar strength (hence, activity), the greater the coke content is and the higher the toxicity of coke molecules. This could be observed with the HMFI zeolite: at low coke contents, T is smaller than 1, which was explained by a competition between reactant and weakly basic coke molecules ("partial poisoning"); at average coke contents, T becomes equal to 1, which is typical of site poisoning and, at high coke contents, T presents values higher than 1, in agreement with pore blockage by very bulky molecules overflowing onto the crystal outer surface. When the acid sites are of different strength, as is the case with the HFAU (HUSY) zeolite, the strongest acid sites, which are the most active, are

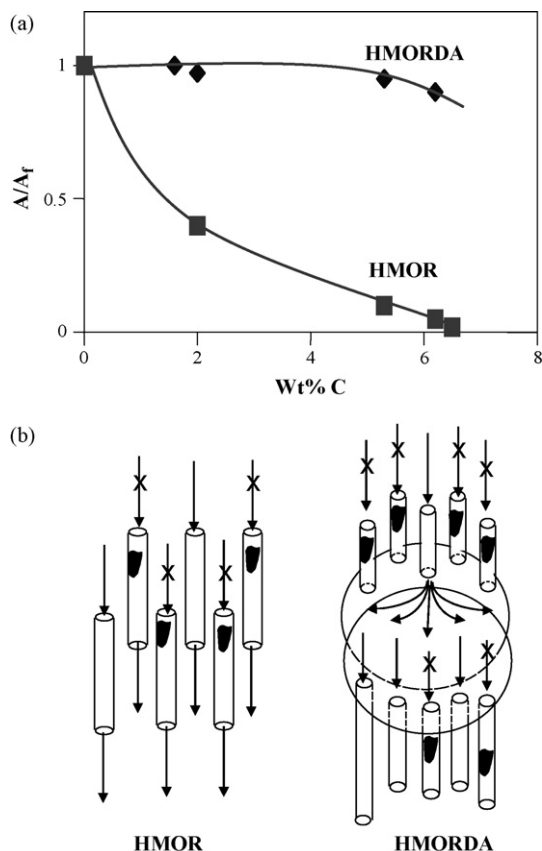


Fig. 20. Creation of mesopores by dealumination of a MOR zeolite and decrease of coke toxicity in methanol conversion: (a) residual activity A/A_f vs. the amount of coke for non-dealuminated (HMOR) and dealuminated (HMORDA) mordenite samples; (b) diffusion of reactant molecules in the channels of HMOR and HMORDA samples.

the first to become deactivated with a consequent apparent high value of the deactivating effect of the first coke molecules formed. The increase in coke content causes a decrease of the apparent toxicity, owing to opposite effects of the development of pore blockage and the decrease in acid strength of the acid sites. This latter change had a predominant effect with the chosen HFAU sample.

- With zeolites such as MOR, in which diffusion of reactant molecules is unidirectional, or with zeolites containing trap cages, such as ERI, deactivation is always due to pore blockage and the deactivating effect of coke molecules is very pronounced ($T > 20$). Indeed, one coke molecule located in a large channel of HMOR is enough to block the access of the reactant molecules to all the acid sites located in this channel (Fig. 20b). Similarly, the coke molecules trapped within the cages of HERI located near the outer surface of the crystals block the access of the reactant molecules to the acid sites located within the inner cages. In both cases, the acid sites made inaccessible appear to be deactivated.

Besides the pore structure, other features of the zeolite can affect the apparent deactivating effect of coke molecules (T). The effect of a heterogeneous distribution in strength of the acid sites has been underscored above. Furthermore, when considering the deactivation of zeolites with a one-dimensional pore system or presenting trap cages, a significant effect of the crystal size could be expected. Thus, the larger the size of MOR crystals, the longer the channels will be and the higher the T value. Similarly, the larger the size of ERI crystals, the higher the number of inner acid sites apparently deactivated per coke molecule. Therefore, T can be significantly

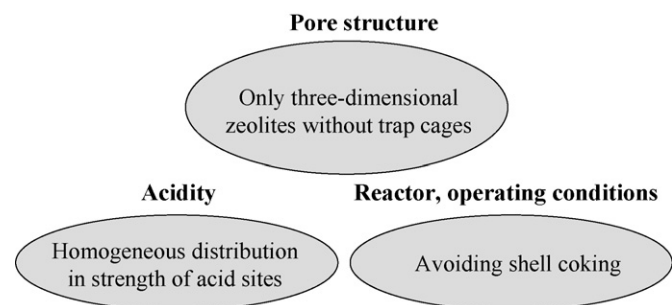


Fig. 21. Guidelines for minimising the deactivating effect of coke.

reduced by operating with small crystal zeolites, e.g. nanosized zeolites. Another way to reduce T is shown in Fig. 20a, on the example of methanol conversion into hydrocarbons over MOR zeolites: dealumination of HMOR decreases more than 10 times the deactivating effect of coke, which can be explained by the creation of inner mesopores which make the pore system quasi-three-dimensional [40].

The operating conditions can also affect, though indirectly, the deactivating effect of coke molecules. Under severe conditions (e.g. high temperature) favouring the desired reaction, there are often diffusion limitations. As a consequence, this reaction and the secondary ones, including coke formation, will occur essentially within the micropores of the outer part of the zeolite crystals and the coke molecules, trapped in these micropores, will block the diffusion of the reactant molecules towards the crystal core, inducing a high T value. This so-called pore mouth (or shell) blockage [41] was shown in methylnaphthalene transformation over a USHY zeolite [15].

7. Guidelines for minimising the deactivating effect of coke

From the effects that the pore system and acidity of the zeolite and the operating conditions have on the rate of coking, general rules for minimising the deactivating effect of coke molecules can be setup. The most important are reported in Fig. 21.

8. Conclusions

The deactivation of most solid catalysts is mainly due to the deposition of heavy secondary products generally designated as coke. Whatever the catalyst employed, the knowledge of coke composition (i.e., the quantitative distribution in nature and size of the components) is of primary importance for establishing the modes of coking and deactivation. Zeolites are the only catalysts for which the composition of coke can be easily determined. Indeed, the zeolite coke molecules are not very bulky, owing to severe steric limitations of their growth in the nanosized pores in which they are essentially formed and trapped.

A simple, although somewhat laborious method was developed and used for several zeolites employed in various acid-catalysed reactions. While the mode of coke formation can be directly drawn from the effect of the zeolite coke content on the coke composition, additional data concerning the effect of coke on the catalytic activity, acidity and accessible pore volume are needed for establishing the mode(s) of deactivation. Although, the methods that were used could be improved (in particular, the different types of acid sites should be distinguished and not considered to be equivalent in strength and activity), the principal modes of coke formation and of deactivation have been clearly established on many examples.

Moreover, the influence of operating conditions, zeolite pore structure and acidity, etc. on the rate of coking and on the deactivating effect of coke molecules was specified. Even if it is often difficult to estimate quantitatively and separately the impacts of acidity and pore structure, it is clear that it is the latter feature that plays the greater role. Both coke formation and deactivation are shape-selective processes.

General rules are proposed for preventing the formation of coke molecules and minimising their deactivating effect. Most of the rules dealing with the optimal choice of reactor, operating conditions and acidity characteristics seem to be valid not only for reactions over acid zeolite catalysts, but also for reactions over non-microporous catalysts.

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