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Deactivation by coking of zeolite catalysts. Prevention of deactivation. Optimal conditions for regeneration

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Abstract

The deactivation of acid zeolite catalysts used in hydrocarbon transformations is mainly due to the deposit inside the pores of heavy secondary products generally known as coke. It is shown how the rate of coking and the deactivating effect of the coke molecules are affected by the pore structure and the acidity of the zeolites as well as by the operating conditions. Directives for minimizing the deactivation by coking are proposed: (1) choice of tridimensional zeolites without trap cavities (large cavities with small apertures); (2) adjustment of the density and strength of the acid sites to the lowest values necessary for the selective formation of the desired products; and (3) choice of operating conditions in order to avoid the formation of coke-maker molecules (alkenes, polyaromatics). The regeneration of zeolites is generally carried out through coke combustion under air or oxygen flow. The detrimental effect that water, produced by coke oxidation, has on the zeolite activity can be limited by using a two-stage generation process, the hydrogen atoms of the coke molecules being oxidized at the low temperature of the first stage.

Keywords: Zeolite catalyst; Coking; Deactivation; Regeneration

1. Introduction

Owing to their remarkable acid properties and their shape selectivity, zeolites are the catalysts most employed in refining (cracking, hydrocracking, hydroisomerization, etc.) and petrochemical processes (alkylation, isomerization and disproportionation of aromatics, etc.) [1,2]. Moreover, zeolites should experience an extensive utilization as catalysts for the synthesis of fine and specialty chemicals [3,4] and for the depollution of industrial and automobile exhausts (elimination of NO_x, of volatile organic compounds, etc.) [5]. Zeolites are also used as adsorbents in many separation and purification processes (isoalkanes from *n*-isoalkane mixtures [6], *p*-xylene from the C_8 aromatic cut [7], etc.).

The deactivation of zeolites observed during these industrial processes can be due to different causes:

1. Poisoning of the active sites either by feed components and impurities, or by non-desorbed heavy products (coke).
2. Blockage of the access of the reactant to the active sites (or of the adsorbate to the pores) by coke, by extra-framework species resulting from dealumination, etc.
3. Structure alterations.
4. Sintering of supported metals (e.g., in bifunctional catalysts).

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Coking is generally the main cause of deactivation of zeolite catalysts [8]. Firstly, coke can poison the active sites or block their access. Secondly, the regeneration of zeolite catalysts requires the removal of coke, generally through oxidative treatment at high temperatures. This treatment has detrimental effects like dealumination and degradation of the zeolite, sintering of supported metals, etc.

In most industrial processes the cost of catalyst deactivation is very high, and mastering catalyst stability has become at least as important as controlling the activity and the selectivity [9]. This is why most contributions to the field of deactivation and regeneration originate in industrial laboratories, much of the related data unfortunately remaining proprietary. Academic laboratories could contribute significantly to this field by developing the basic knowledge indispensable to master catalyst stability and to operate the regeneration under optimal conditions. This is largely the case in the deactivation of zeolite catalysts by coking [8] owing to the development of an efficient method for establishing the coke composition [10]. This method consists of treating the coked zeolites with HF solution in order to dissolve the zeolite and liberate the coke molecules. As most of the acid sites are located in the narrow pores of the zeolites, the coke molecules formed in these pores are relatively simple. Most of these molecules are therefore soluble in organic solvents and the composition of coke (not only the chemical identity of the components but also their distribution as a function of their nature and size) can be obtained. This composition plays an essential role in understanding the modes of coke formation, deactivation and coke oxidation [8]. On the basis of this knowledge, some simple rules are proposed here for limiting the rate of coking of zeolite catalysts and the deactivating effect of coke and for optimizing the conditions of regeneration. Examples chosen in the transformation at high temperatures of hydrocarbons on acid zeolites will be given.

2. How to limit the formation of catalytic coke

Coke results from the transformation of reactant(s), reaction products, impurities of the feed through various successive steps, most of them bimolecular: condensation, hydrogen transfer, etc. Therefore, the rate of coking depends on the parameters which usually affect the rate of catalytic reactions [11,12], namely:

1. The characteristics of the hydrocarbon reactant-active site couple;
2. The characteristics of the zeolite pore structure: in particular the size and the shape of the cavities (or channel intersections) in which are located the acid sites and which can therefore be considered as microreactors; and
3. The operating conditions: temperature, pressure, concentration of the various reactive species.

However, coke has the peculiarity of being a non-desorbed product. Therefore, its formation, besides the reaction steps requires the coke molecules to be retained inside the zeolite pores or on the outer surface of the crystallites. This retention occurs because coke molecules are not volatile enough to be eliminated from the zeolite under the operating conditions or because their size is greater than the pore aperture (trapping in the cavities or at channel intersections). This second cause of retention is predominant at temperatures >300°C [13], range of temperature corresponding to most of the refining and petrochemical processes. In this case the main parameter determining the retention of coke molecules is the difference between the size of the cavities (or of the channel intersections) and the size of the pore apertures. The greater the difference the easier the trapping.

2.1. *Nature of the reactant and coking rate*

On acid catalysts, coking occurs rapidly from alkenes and polyaromatics or reactants undergoing a rapid transformation into these coke-maker molecules [11]. On the other hand, it occurs slowly from the reactants such as linear alkanes or monoaromatics whose transformation into alkenes or polyaromatics is slow. Thus, at 450°C on a USHY zeolite, coking occurs more or less at the same rate from propene, cyclohexene and methylnaphthalene, but slightly slower from cumene which cracks easily into benzene and propene, 10 times slower from toluene and *n*-heptane and 100 times slower from benzene. No coke is directly formed from cumene or from *n*-heptane as shown by the absence of coking without cracking (for instance, at low temperature).

A satisfying correlation was found by Appleby et al. [14] between the amount of coke deposited on silica alumina and the basicity of the aromatic reactant: the greater the basicity the faster the coke formation. However, this correlation does not apply to alkenes which although slightly basic are coke makers. The rapid formation of coke from alkenes and polyaromatics are therefore due to different reasons: strong adsorption on the acid sites in case of polyaromatics, great reactivity of the adsorbed species (carbenium ions) formed from alkenes [11].

2.2. *Pore structure and coking rate*

Since bimolecular reactions between bulky molecules (condensation, hydrogen transfer) are involved, steric constraints limit the formation of coke molecules in the zeolite pores. These constraints allow to explain why in FCC the selectivity to coke of Y zeolite catalysts is lower than that of silica alumina catalysts [15]. They could also explain why the selectivity to coke (expressed in grams of coke formed per 100 g of alkane converted during the transformation at 427°C of a mixture of *n*-hexane, 3-methylpentane, 2,3-dimethylbutane, benzene and toluene at similar total conversion levels) is equal to about 1 with large pore zeolites, 0.1 with average pore zeolites and 0.05 with small pore zeolites [16]. Different results are found during *n*-heptane cracking at 450°C on four protonic zeolites presenting the same initial activities: the initial coking/cracking rate ratio is equal to about 1 with HERI and HMOR, 4 times lower with USHY and 1000 times lower with HZSM5 [17]. The high selectivity to coke of HERI, a small pore zeolite, was attributed to a rapid blockage of coke molecules or of their precursors in the trap cavities of this small pore zeolite. On the other hand, the very slow rate of coking found with HZSM5 would be due to the low density of its acid sites rather than the average size of its pores. Indeed, the coking/cracking rate ratio is only 2 times greater on a dealuminated HY zeolite with a density of strong acid sites close to that of HZSM5 [18]. The effect of the pore structure on the coking selectivity therefore seems more limited than the effect of acidity and particularly the acid site density.

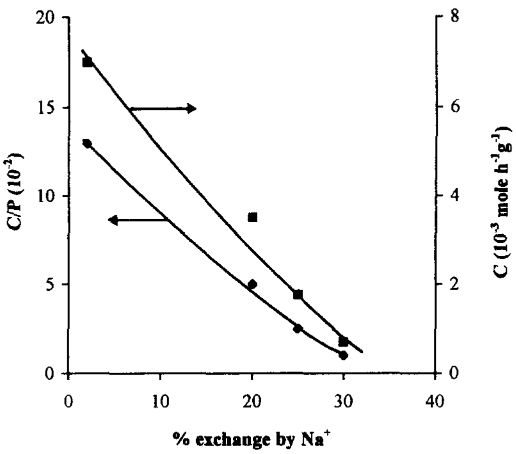

Fig. 1. Coking rate (C) and coking/cracking rate ratio (C/P) during *n*-heptane cracking at 450°C on USHY zeolites as a function of the percentage of exchange by sodium cations.

2.3. *Acidity and coking rate*

As shown in the literature, the rate of coking and the selectivity to coke (for instance the coking/desired reaction rate ratio C/P) depends a lot on the strength and density of the acid sites. Thus, the rate of coke formation during *n*-heptane cracking at 450°C on USHY exchanged by sodium cations and the coking/cracking rate ratio (C/P) decrease with increasing sodium content (Fig. 1), which can be attributed to both a decrease in the strength and in the density of the acid sites [17]. The positive effect of the density of the acid sites on the C/P ratio is clearly demonstrated in the case of dealuminated HY zeolites having similar acid strength [19]. Moreover, this ratio is greater when the dealuminated Y samples present extra-framework species, which has been related to an increase in the strength of the protonic sites of the zeolites caused by their interaction with the extra-framework aluminium Lewis species [19].

2.4. *Operating conditions and coking rate*

The rate of coking depends on the operating conditions and, in particular, on the reaction temperature T [11,12]. During the transformation of alkenes (propene, cyclohexene, etc.) on various zeolites (USHY, HZSM5, etc.) it has been found that the rate of coking passed through a minimum [8,11]. This complex behaviour can be related to the fact that coking requires, besides reaction steps, the retention of coke precursors and coke molecules inside the pores and that both the nature of the chemical steps and the cause of trapping in the pores depend on *T*. From *n*-heptane the rate of coking increases with *T*, hence with the rate of cracking into alkenes (which are coke-maker molecules). Practically no deactivation (hence no coking) occurs when the transformation of ethylbenzene [20] and cumene [21] are carried out at temperatures low enough to avoid the formation of alkenes through dealkylation.

The rate of coking increases generally with the reactant pressure. Thus in *m*-xylene disproportionation on mordenites [22] the coking rate and the coking/disproportionation rate ratio for $P_{m\text{-xylene}}=0.2$ bar were about 2 times greater than for $P_{m\text{-xylene}}=0.06$ bar. The use of hydrogen in the feed was found to decrease the formation of coke and to improve the zeolite stability for typical reactions of acid catalysis such as toluene [23] and cumene disproportionation [24]. The effect is generally more pronounced when hydrogen is used at high pressure or activated by redox compounds. Obviously, the formation of coke is still more significantly reduced when there is a change from an acid to a bifunctional mechanism.

2.5. *General rules for limiting the formation of coke*

From this effect the zeolite characteristics and the operating conditions on the rate of coking, general rules can be set up for limiting the formation of coke. The most important are indicated in Table 1.

3. How to minimize the deactivating effect of coke

The modes of deactivation of the zeolite catalysts were established during *n*-heptane cracking at 450°C on protonic zeolites with different structures: monodimensional or tridimensional – small, average or large pore apertures – tubular or with cavities [13]. Deactivation could be due to: (a) a limitation of the access of the reactant to the active sites of a cavity or a pore intersection in which is located a coke molecule, or (b) a blockage of the access; (c) and (d) a limitation or a blockage of the access of the reactant to the active sites of cavities, of pore intersections or parts of channels in which coke molecules are not located.

In modes a and b the limitation or the blockage are either due to steric reasons, namely the diffusion of the reactants in the cavity or at the pore intersections is limited or blocked, or chemical reasons – the coke molecules are reversibly or quasi-irreversibly adsorbed on the acid sites (site coverage) [25]. With these modes the deactivation of the zeolite is generally limited since only the sites located in the cavity or at the channel intersection (often only one site) are partially or totally deactivated.

Modes c and d correspond to what is generally called pore blockage [25]. With these modes the deactivating effect of the coke molecules is very pronounced, because a large number of active sites are generally located in the inner pores. The access of the reactant to these pores is limited or blocked.

With tridimensional zeolites having no trap cavities such as Y and ZSM5 only site coverage (modes a and

Table 1
General rules for limiting formation of the coke

Choice and adaptation of the pore structure
Space available near the active sites: large enough to allow the main reaction but narrow enough to limit the formation of coke by steric constraints
Diffusion path (size of the pore apertures, of the crystallites, etc.) allowing a rapid diffusion of coke precursors (in particular, no trap cavities)
Adjustment of the acidity
Lowest density and weakest strength of the acid sites necessary for the selective formation of the desired products
Choice of the operating conditions
Conditions avoiding the formation of coke-makers side products (alkenes, polyaromatics)
Use of hydrogen (under pressure and/or activated by redox compounds) for reducing the concentration in coke precursors

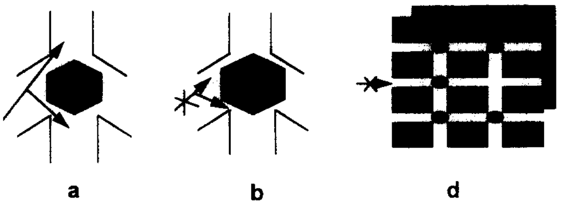

Fig. 2. Modes of deactivation of a zeolite with interconnecting channels and without cavities (e.g., HZSM5). (a and b) Site coverage; (d) pore blockage.

b) is observed at low coke content while pore blockage appears at high coke content caused by coke molecules located on the outer surface of the crystallites (Fig. 2). Therefore, with HZSM5 whose acid sites are of identical strength the greater the coke content the greater the deactivating effect of coke molecules. The situation is more complex when the acid sites of the zeolites are of different strengths as is the case with HY zeolites. Indeed, the strongest acid sites, hence the most active, are the first to be deactivated, resulting in a large deactivating effect of the coke molecules at low coke content [13].

With monodimensional zeolites such as HMOR or with zeolites presenting trap cavities (large cavities with small apertures) such as HERI, the deactivation occurs only through pore blockage. With HMOR, one coke molecule located in the large channel (most likely at the intersection of this channel with the narrow pores inaccessible to the organic molecules) is able to block the access of the reactant to all the active sites located in the channel resulting in a large deactivating effect of the coke molecules. This large deactivating effect is also observed with HERI because the coke molecules initially formed, located in the cages near the outer surface, limit and then block the access of the reactant to the inner cages [13].

The pore structure of the zeolite is therefore the main parameter which determines the deactivating effect of coke molecules. Hence, only tridimensional zeolites without trap cavities could be used as catalysts for reactions in which coke can be rapidly formed because of the presence of coke-maker molecules and operating conditions favouring coke formation. However, monodimensional zeolites or zeolites with trap cavities could be stable catalysts for processes in which the formation of coke is very slow. A typical example is *n*-hexane isomerization on a bifunctional PtHMOR catalyst [26]. Modifications of the pore structure can also significantly decrease the deactivating effect of coke molecules. This has been shown, in particular, for the transformation of methanol to short-chain olefins on HMOR catalysts; the deactivating effect of coke molecules is much lower (>10 times) in dealuminated samples because mesopores created by dealumination allow a quasi-tridimensional diffusion of reactant molecules [27].

Besides the pore structure, the operating conditions can also affect, though indirectly, the deactivating effect of coke molecules. With operating conditions favouring a rapid formation of coke, coke molecules will be formed and deposited in the pores of the outer part of the zeolite crystallites even if the zeolite is not monodimensional and has no trap cavities. These coke molecules block the diffusion of the reactant molecules to the acid sites of the core of the crystallites, with a large deactivating effect of coke molecules. This pore mouth (or shell) blockage [28] was shown in methylnaphthalene transformation on a USHY zeolite [11].

Some general rules allowing to minimize the deactivating effect of coke are indicated in Table 2.

4. Optimal conditions for removal of coke

The removal of coke from deactivated catalysts, sometimes with the addition of oxygen, is generally

Table 2
General rules for minimizing the deactivating effect of coke

Choice (or adaptation) of the pore structure: Tridimensional zeolites without trap cavities (large cavities with small apertures) must be employed
Adjustment of the acidity: Homogeneous distribution in strength of the acid sites
Choice of operating conditions avoiding shell blockage

carried out through an oxidative treatment under air flow. The choice of the operating conditions (and, in particular, of the temperature) is important for limiting the detrimental effect the water, produced by coke oxidation, has on the zeolite catalyst; dealumination, structure alteration, etc. [29].

Whatever the zeolite and the coke content, the oxidation of the coke molecules begins by their hydrogen atoms with formation of oxygenated compounds [30–33]. Subsequently, these oxygenated compounds can undergo decomposition leading particularly to CO and CO_2 or complete oxidation into CO_2 and H_2O. A more complete description of the reactions and the intermediates involved in coke oxidation on HY zeolites has been recently made by Moljord et al. [34]. Firstly, these authors have shown that the oxidation of pyrene introduced in the supercages by simple impregnation of the Y zeolites could be considered as a model reaction for coke oxidation. In particular, temperature had the same effect on the production of CO, CO_2 and H_2O during the oxidative treatment of HY zeolites whether impregnated with pyrene or coked. The method used to recover the coke from the zeolite [10] was employed to recover the products of partial oxidation of pyrene. From their analysis through GC–MS it was concluded that, besides the complete oxidation, three main types of reactions participated in the oxidation of pyrene and in that of coke as follows:

1. Formation of oxygenated compounds by partial oxidation of polyaromatics which begins at a low temperature (160°C).
2. Condensation above 250°C of the polyaromatic components of coke and their oxidation products with formation of highly polyaromatic compounds.
3. Decarbonylation and decarboxylation of oxygenated compounds which occurs only above 300°C.

Since a large amount of the hydrogen atoms of coke molecules are oxidized at a low temperature, a simple solution for limiting the degradation of the zeolite is to operate the removal of coke in two stages, the first one at a low temperature and the second one at a high temperature. Two-stage regeneration is now largely introduced in FCC units minimizing the degradation of the catalyst by avoiding its contact with steam at a high temperature [29].

With pure acid zeolites the density of the acid sites seems to be the main parameter determining the rate of coke oxidation. Radical cations formed through reaction of molecular oxygen on coke molecules adsorbed on protonic sites were proposed as intermediates in coke oxidation [35]. The pore structure of the zeolite and the coke content have only a limited effect on the rate of coke oxidation. Combustion accelerators (such as platinum or palladium) can be introduced in low amounts in the zeolite catalysts in order to obtain an easier elimination of coke and to convert CO, thus produced, into CO_2. This is generally done in FCC catalysts with the advantages of a greater activity of the regenerated catalysts, a shorter residence time in the regenerator and no need for a CO afterburner [29]. A lower temperature for complete removal of coke from zeolite catalysts can also be expected with a less detrimental effect of regeneration.

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