Influence of carbonaceous deposits on the acidity of a zeolite with two non-interconnected pore systems: MCM-22

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H-MCM-22 zeolite samples used in *n*-heptane cracking at 450 °C for time-on-stream between 2 min and 100 h, hence with different coke contents (from 0.45 to 6.9 wt%), were characterized by FTIR spectroscopy before and after pyridine adsorption. As is observed with the zeolites with only one pore system, coke molecules interact preferentially with the most acidic hydroxyl groups, which is confirmed by the large decrease in the number of the protonic sites able to retain pyridine adsorbed at high temperature. A decrease in the number and strength of the Lewis acid sites able to retain pyridine adsorbed is also observed above 0.5 wt% coke, which can be related to blockage by coke of the access of pyridine molecules to the supercage pore system.

KEY WORDS: MCM-22 zeolite; FTIR spectroscopy; deactivation by coking; Brønsted and Lewis acidity

1. Introduction

MCM-22 zeolite has the particularity to present two non-interconnected pore systems. The first one which is tridimensional consists of large supercages (7.1 Å ∅, 18.4 Å) with relatively small apertures (4.0 × 5.5 Å), the second one of interconnected sinusoïdal channels (4.0 × 5.0 Å) [1].

We have recently shown that for *n*-heptane cracking over several H-MCM-22 samples there is a rapid blockage by carbonaceous deposits ("coke") of the access of the reactant molecules to the supercages with as a consequence a very fast initial deactivation followed by a plateau in activity [2]. Therefore, it can be considered that on the fresh zeolite, *n*-heptane cracking occurs in both pore systems whereas at the plateau, it occurs only on the protonic sites of the sinusoïdal channels.

IR spectroscopy is one of the first techniques used to investigate the nature of carbonaceous deposits (named "coke" in this study) formed and retained inside the pores of zeolites during hydrocarbon reactions [3]. This technique was extensively used by various authors and particularly by Karge and coworkers for characterizing coke formed from alkenes over acidic zeolite catalysts [4]. The bands observed at low temperatures (25–100 °C) corresponded mainly to paraffinic species and to a small extent to olefinic or polyolefinic species. At high temperatures ($>$250 °C), the bands of coke (intense band at 1585 cm^{-1}, weak band around 3080 cm^{-1}) corresponded predominantly to alkylaromatic and polyaromatic species [4]. However, the information obtained by this non-destructive technique is not enough to deduce the composition of coke, that is to say the exact nature of coke components and their distribution.

As it was emphasized [5], the only way to determine the chemical composition of carbonaceous deposits is to totally separate them from the zeolite (for instance by dissolution of the zeolite in a solution of hydrofluoric acid [6]) and then to analyze them by appropriate techniques (GC/MS, etc). This destructive method is very suitable for establishing the composition of coke formed at low temperatures and also at short time-on-stream (low coke contents) at high temperatures; the composition of the highly polyaromatic coke formed at long time-on-stream (high coke contents) cannot be established [5].

However, complementary information can be obtained from the characterization of coked zeolite samples by IR spectroscopy [4]. Firstly, the amount of coke deposited on the zeolite can be estimated. Indeed the absorbance of the so-called "coke band" in the CH deformation region around 1600 cm^{-1} is generally found to be directly proportional to the amount of coke deposited on the sample [7,8]. Secondly, the interactions between coke molecules and protonic sites (hydroxyl groups) can be detected. This information is particularly useful in order to discriminate between the modes of deactivation. When deactivation occurs by site poisoning the number of protonic sites in interaction with coke molecules should be close to the number of coke molecules; when it occurs by pore blockage, the former is much lower than the latter. This latter situation was observed during ethylbenzene transformation over H-MOR [4]. Lastly, indirect information on the effect of coke on acidity can also be obtained by investigating base (generally pyridine) adsorption on the coked samples. It is from this type of experiments that the inactivity of Lewis acid sites for coking previously demonstrated by comparing dehydroxylated and non-dehydroxylated zeolites [9] was confirmed [8,10].

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In this paper, all the above described IR methods of characterization of coked samples are used to specify the effect of coke deposits on the acidity of a H-MCM-22 sample (total Si/Al = 30, M-30) used for n-heptane cracking at 450 °C and to confirm the mode of deactivation previously proposed.

2. Experimental

The fresh and coked H-MCM-22 samples have been previously described in [11] and [2], respectively.

For IR studies, the samples were pressed into thin wafers (5–15 mg cm^{-2}). The wafers were pretreated at 200 °C in vacuum (1.3×10^{-4} Pa) for 1 h. An excess of pyridine (267 Pa in the gas phase), previously dried over 4A molecular sieve, was adsorbed at 150 °C and after 15 min physisorbed pyridine was removed by 1 h evacuation at the same temperature. All the IR spectra were recorded at room temperature.

3. Results and discussion

The conversion of n-heptane decreases rapidly during the first minutes of reaction and remains practically constant after 2 h reaction. Deactivation can be related to coke formation (figure 1). Coke is rapidly formed during the first minutes of reaction: 0.45 wt% deposited on the zeolite in the first 2 min, then more slowly, e.g., 4.3 wt% deposited from 2 to 100 h, i.e., 400 times more slowly than initially. The initial period of deactivation can be attributed to blockage by coke of the access to the protonic sites of the supercages, the plateau in activity to n-heptane cracking in the sinusoïdal channels [2].

IR spectra of coked samples show the presence of various bands corresponding to carbonaceous deposits: a massif (A_1) between 1560 and 1640 cm^{-1}, a second one (A_2) between 1300 and 1400 cm^{-1} with approximately the same intensity and a third one, 15 times less intense, between 2860 and 3100 cm^{-1}. An increase with coke content in the intensity of the main bands is observed (figure 2). However, contrary to what is found with many zeolites [8,10,12], the absorbance of the massif (A_1) between 1560 and 1640 cm^{-1} (generally called the coke band) is not proportional to coke content (figure 3). This indicates a very significant and unusual change in the composition of coke as was furthermore previously shown [2]: at low coke contents mainly methylpolyaromatic molecules with 4–6 aromatic rings, at high coke contents mainly highly polyaromatic molecules (probably with methyl groups) and also naphthalene molecules. The increase with coke content in the amount of naphthalene molecules which, in this “two in one” zeolite, are formed in the sinusoïdal channels, probably explains that no proportionality is found between the intensity of the “coke band” and the coke content (figure 3).

Figure 4(A) shows that coke molecules interact with all the hydroxyl bands: the band at 3620 cm^{-1} with a shoulder at 3580 cm^{-1} which corresponds to bridged hydroxyl groups located in supercages and in sinusoïdal channels, the band at 3665 cm^{-1} which corresponds to hydroxyl groups linked to extraframework Al species (EFAL) and the bands

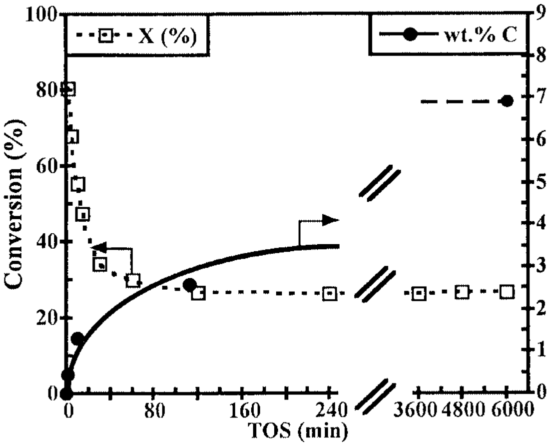


Figure 1. Conversion of n-heptane and percentage of coke deposited on the zeolite as a function of time-on-stream (TOS). Weight hour space velocity WHSV = 2.74 h^{-1}.

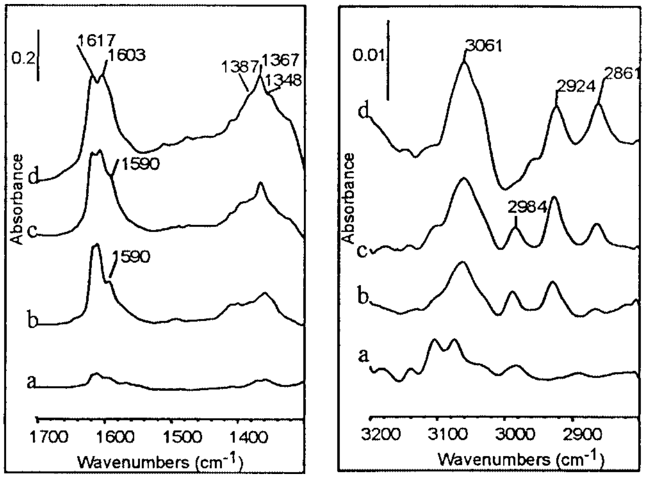


Figure 2. IR spectra of coke deposited on the H-MCM-22 sample for various zeolite coke contents: (a) 0.45, (b) 1.3, (c) 2.6 and (d) 6.9 wt% C.

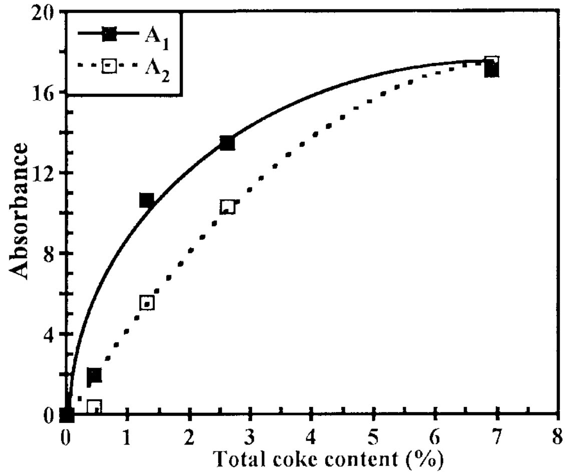
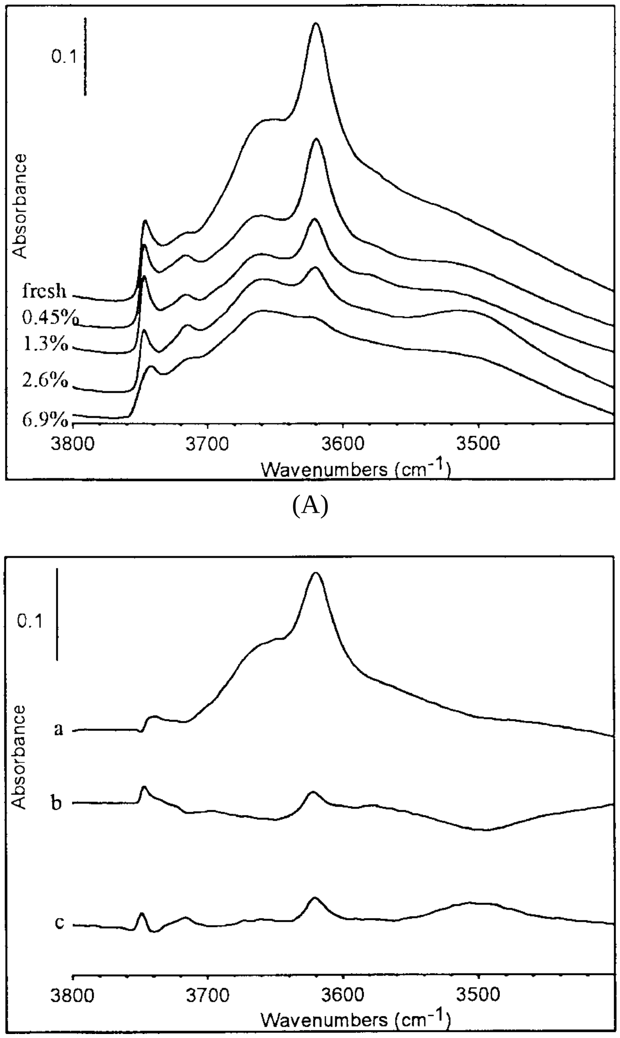


Figure 3. Absorbance of the coke bands versus coke content. A_1 massif 1560–1640 cm^{-1} and A_2 massif 1300–1400 cm^{-1}.

at 3730 and at 3745 cm^{-1} corresponding to external silanol groups. The band at 3620 cm^{-1} related to the protonic acid sites of the zeolite is very affected at low coke contents. However, it is also the case for the hydroxyl groups linked to EFAL species which, however, did not interact with pyridine species [12]. This can only be explained if pyridine molecules cannot have access to the hydroxyl groups whereas the slimmest *n*-heptane molecules could. Furthermore, at high coke contents, external silanol groups interact with coke molecules, most likely with the highly polyaromatic coke components. This suggests that these coke components are located (or overflow) on the outer surface of the zeolite crystallites as it is the case with other zeolites [13].



(A)

(B)

Figure 4. (A) Hydroxyl bands of fresh and coked samples and (B) difference spectra: (a) fresh − coked 1.3 wt%, (b) coked 1.3 wt% − coked 2.6 wt%, (c) coked 2.6 wt% − coked 6.9 wt%.

The difference spectra represented in figure 4(B) confirm the conclusions drawn from figure 4(A). Moreover, the presence of negative bands indicates the appearance of new bands by shift of the original ones. Thus in figure 4(B-b), the negative band at 3650 cm^{-1} is due to the shift of the silanol bands, the one at 3500 cm^{-1} to the shift of acidic hydroxyl groups. The disappearance at high coke contents of this latter band (figure 4(B-c)) is probably related to the large change in the coke composition.

Pyridine adsorption results in a decrease in the intensity of the IR bands corresponding to coke molecules (figure 5). This is shown by the decrease in the intensity of the bands at 1400 and 1365 cm^{-1} which do not overlap on the bands of pyridine but also by the quasi-identical intensities of the band at 1617 cm^{-1} which overlaps with the pyridine band (figure 5). The decrease in intensity of the coke bands (massifs at 1560–1640 and 1300–1400 cm^{-1}) was estimated; obviously participation in the massifs of the pyridine bands was subtracted. Table 1 shows that the decrease in intensity caused by pyridine adsorption is the same for both massifs, passing from approximately 25% at low coke contents to 2–8% at high coke contents. Therefore, pyridine is able to desorb coke molecules from the acid sites, the effect being, as expected, more pronounced for the less polyaromatic coke molecules.

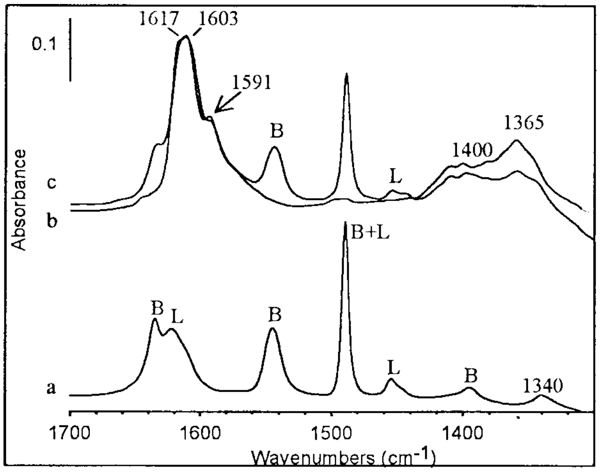


Figure 5. IR spectra of the fresh zeolite after pyridine adsorption (a) of the 1.3 wt% coked zeolite before (b) and after (c) pyridine adsorption.

Table 1
Influence of pyridine adsorption on the intensity of the coke bands.

Coke content	Massif A_1 (1560–1640 cm^{-1})[a]			Massif A_2 (1300–1400 cm^{-1})		
(wt%)	A_b	A_a	ΔA (%)	A_b	A_a	ΔA (%)
0.45	2.65	1.95	26	1.05	0.8	24.5
1.3	11.45	8.55	25.5	7.1	5.4	24
2.6	14.85	12.75	14	11.3	9.35	17.5
6.9	17.51	17.11	2	16.5	15.2	8

[a] A_b, A_a absorbances of the massifs before and after pyridine adsorption; ΔA decrease in the absorbance.

Table 2

Concentrations and acid strengths of the Brønsted and Lewis acid sites in the fresh and coked zeolite samples.

Coke content (wt%)	Brønsted sites			Lewis sites	
	Concentration C_{B0} (μmol g^{-1})	Consumed sites ΔC_B (μmol g^{-1})	C_B/C_{B0}	Concentration C_{L0} (μmol g^{-1})	Consumed sites ΔC_L (μmol g^{-1})
0	328	0	0.70	43	0
0.45	299	29	0.47	47	0
1.3	280	48	0.49	26	17
2.6	194	134	0.32	29	14
6.9	115	213	0.095	23	20

The concentrations of the Brønsted and Lewis acid sites (C_{B0} and C_{L0}) were estimated in the fresh and coked samples from the intensities of IR bands after desorption at 150 °C, corresponding to pyridine molecules adsorbed on these sites (1545 and 1450 cm^{-1}) by using the previously determined extinction coefficients [14]. The ratio between the concentrations of the pyridinium ions after desorption at 350 and 150 °C was taken as an estimation of the strength of the Brønsted sites (C_B/C_{B0}, table 2). The apparent effect of coke on C_{B0} is very limited especially at low coke contents. Thus, for 1.3 wt% coke, the number of protonic sites apparently consumed (table 1) is equal to the number of coke molecules (53 μmol g^{-1}) estimated from the coke composition. This suggests a deactivation by site poisoning although deactivation was shown to be due to pore blockage [2], hence that more than one protonic site should be deactivated per coke molecule. This too low "toxicity" of coke molecules is probably due to the desorption of coke molecules from the acid sites caused by pyridine (figure 5). This displacement of coke molecules by pyridine explains also why C_{B0} decreases from 194 to 115 μmol g^{-1} when the coke content increases from 2.6 to 6.9 wt% although no decrease in activity is observed (figure 1). This decrease in C_{B0} would be only due to the decrease in the desorption of coke molecules: from approximately 15% at 2.6 wt% coke to practically 0% at 6.9 wt% coke (table 1). Furthermore, at high coke contents, C_{B0} should be representative of protonic sites in the sinusoïdal channels. This is practically verified for 6.9 wt% coke. Indeed C_{B0} (115 μmol g^{-1}) is close to the number of protonic sites in the sinusoïdal channels (138 μmol g^{-1}) estimated in a previous study [11]. Other important information shown in table 2 is the decrease in C_B/C_{B0} which indicates that deactivation has affected the strongest protonic sites, as it is well demonstrated with various zeolites [15]. This is in agreement with the previous conclusion that the strongest protonic sites are located in the supercages and that their deactivation by pore blockage is very fast. However, the value of C_B/C_{B0} found at 6.9 wt% coke is lower than the one found for the protonic sites in the sinusoïdal channels of the fresh zeolite [11]. No clear explanation can be proposed for this observation.

A decrease in the apparent concentrations of Lewis acid sites (C_{L0}, table 2) is also observed, even at low coke contents, whereas with most of the zeolites this occurs at high coke contents only. However, as the decrease in C_L in the other zeolites is due to pore blockage and not to poisoning of Lewis sites by coke [9,10,12], the particular behaviour of H-MCM-22 can easily be explained by the development of pore blockage at low coke contents.

4. Conclusions

From this characterization of coked H-MCM-22 samples by IR techniques, the following conclusions can be drawn:

(1) Contrary to what is observed with most of zeolite catalysts, the intensity of the coke band at approximately 1600 cm^{-1} is not proportional to coke content. This observation could be due to the particular change in coke composition in this zeolite with two non-interconnected pore systems.

(2) Coke molecules interact with the different types of hydroxyl groups, even with the hydroxyl groups linked to extraframework aluminium species which are neither acidic nor accessible to pyridine molecules.

(3) Pyridine adsorption causes a desorption of part of coke molecules from the protonic sites; this desorption being more pronounced at low than at high coke contents. This desorption introduces a lack of precision in the estimation of the effect of coke molecules on the acidic sites.

(4) As is observed with many other zeolite catalysts, coke molecules cause a decrease in the number of protonic sites able to retain adsorbed pyridine as well as in their strength. However, a decrease in the number of Lewis sites able to retain adsorbed pyridine is also observed from low coke contents, which indicates a blockage of their access.

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