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Catalytic transformation of cholesterol over HFAU zeolites

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Abstract

The catalytic behavior of an HFAU zeolite was studied in the transformation of cholesterol, the most abundant sterol in the animal kingdom. It was found that such a catalyst is very active as of a temperature of 25 °C. After 1 h of reaction, about 50% of cholesterol was converted and 95% were transformed after 5 h. The first occurring reaction is dehydration leading cholestadienes as primary products. The secondary compounds arising from the transformations of cholestadienes identified in the reactional middle are cholestenes, diacholestadienes, spirocholestadienes and aromatics. On the other hand, among the trapped compounds in the cavities, it was identified oxygenated compounds (mono- and dioxygenated molecules) and aromatics, too. A synthetic scheme of cholesterol transformation over HFAU zeolite at ambient temperature was proposed from the evolution of identified reaction products.
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Keywords: Cholesterol; Alcohol dehydration; HFAU zeolite

1. Introduction

The progressive depletion and rise in price of the fossil fuels means that alternative energy sources must be considered. Among them, the renewable biomass is an option which could be economically attractive. Biomass such as ethanol can be directly used as direct energy source, but it would seem more rational to transform biomass into interesting products (fuel, intermediate compounds, etc.).

In this way, cholesterol, which is the most abundant sterol in the animal kingdom and also present in all plant lipids, can be valorised firstly into cholestadiene by dehydration over heterogeneous acid catalysts. On the other hand, steroids (like cortisone and its derivatives) have been fertile fields for synthetic chemists since the structures of representative members of this important class of natural products have been elucidated in the 1930s. If it can be fairly stated that almost every synthetic method was tested in the steroid area, there is a few number of reports, to our knowledge, on the reactivity of such a class of compounds with zeolites [1–4].

Alcohol dehydration reactions generally occur in presence of strong acid such as H_2SO_4, $KHSO_4$ or H_4PO_4. The conditions are drastic for primary alcohol (concentrated H_2SO_4, 170–180 °C), milder for secondary and tertiary alcohol (diluted H_2SO_4, 80–90 °C). Solid acid catalysts can be used for alcohol dehydration. Thus, heteropolyacids (HAP) were used for alcohol dehydration of ethanol [5–7], butan-1-ol [8], 1,2-diphenylethanol, 1-(3,4-dimethoxyphenyl)-2 phenylethanol and cholesterol [9]. Zeolite catalysts, due to their acidic properties [10], have been also used in dehydration reaction of alcohols [11–15]. However, this reaction over zeolite has often concerned low molecular weight alcohols ($<C_6$).

In this work, the catalytic transformation of cholesterol was studied at 25 °C over an acidic type of Faujasite zeolite (HFAU). Then, the aim of this work is the description of the compounds resulting from the transformation of the cholesterol in the presence of large pore HFAU zeolite. Furthermore, some mechanisms explaining the formation of the main reaction products will be proposed. This study concerning the catalytic transformation of cholesterol over this acidic zeolite is one of the first experiment with such compounds that could be extended to the other classes of steroids.

As, it was already shown that cholesterol can be adsorbed in the internal pore of NaY zeolite [4] this complex molecule with

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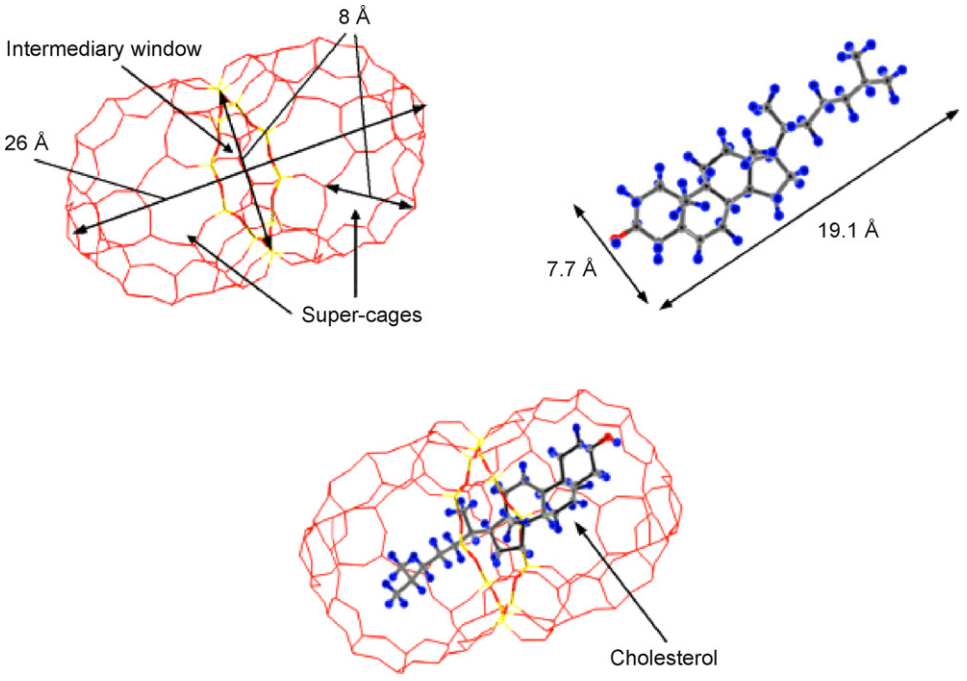


Fig. 1. Molecular modeling of HFAU zeolite, cholesterol and cholesterol in zeolite performed with the Accelrys Cerius 2 software.

an average size of 7.7 Å × 19.1 Å can be included in the cavities of Faujasite-type zeolite (Fig. 1) and reaction can occur for a large part in the internal pores of this large pores zeolite. However, as it shown in Fig. 1 that one cholesterol molecule occupies two super-cages, the effective diffusivity inside the pore must be relatively slow.

2. Experimental

2.1. Catalyst characterization

Large pore Faujasite zeolite (HFAU) was supplied by PQ zeolites (CBV720). This zeolite was commercially obtained after successive steaming and acid leaching of NH_4FAU zeolite. The physicochemical characteristics of this sample are reported in Table 1.

The framework Si/Al ratio was close to 15 and now catalyst will be named HFAU(15). The number of framework aluminium per unit cell (N_{Al}) was estimated from the unit cell parameters a_0 by using the equation proposed by Breck and Flanigen [16], $N_{Al} = 115.2$ ($a_0 = 24.191$). The unit cell formula and the number of extraframework aluminium species per unit cell (EFAL) were determined from the elemental composition and from N_{Al}. Nitrogen adsorption measurements were performed at −196 °C with the gas adsorption system ASAP2000 (micromeritics). The micropore volume was equal to 0.344 $cm^3\,g^{-1}$ and this dealuminated zeolite possess some mesopores (0.163 $cm^3\,g^{-1}$) which certainly allow a best diffusion and desorption of cholesterol and reaction products. The surface area of this zeolite measured in the same conditions was equal to 827 m^2/g and the external surface was about 76 m^2/g. The zeolite crystal size was estimated by scanning electron microscopy and was close to 0.5 μm. The acidity of the samples was estimated by adsorption of pyridine followed by infrared (IR) spectroscopic measurements. The zeolites were pressed into thin wafers (5–15 mg/cm^2). The wafers were pretreated at 200 °C in a vacuum (1.33×10^{-4} Pa) for 1 h. An excess of pyridine was adsorbed at 150 °C, and after 5 min of contact, physisorbed pyridine was removed by evacuation for 1 h at the same temperature. The concentration of Brönsted and Lewis sites able to retain pyridine adsorbed at 150 °C were determined from the absorbance area of the bands at 1545 and 1450 cm^{-1}, respectively, using extinction coefficients previously determined [17]. Thus, acidity measured by pyridine adsorption followed by IR shows the presence of a large quantity of Brönsted acid sites (327 mmol g^{-1}).

Molecular modelisations presented in Fig. 1 were performed with the Accelrys Cerius 2 software.

Table 1
Physicochemical characteristics of HFAU zeolite

Zeolite	Reference	Unit cell formula	(Si/Al) framework	Crystallites size (μm)	Surface area (m^2/g)		Pore volume ($cm^3\,g^{-1}$)		Acidity (μmol g^{-1})	
					Global	External	Micro	Meso	Brönsted	Lewis
HFAU(15)	CBV720	$Na_{0.3}H_{11}Al_{11.3}Si_{180.7}O_{384}$ 2.3 EFAl[a]	15	0.5	827	76	0.344	0.163	327	74

[a] EFAl: extraframework aluminium species.

2.2. Cholesterol transformation

The transformation of cholesterol was carried out in batch reactor at 25 °C. Before reaction, the catalyst was tasselled and crushed to 0.2–0.4 mm size and activated in situ at 500 °C under dry air flow (60 ml min^{-1}) overnight, then cooled down to the reaction temperature under nitrogen flow. Afterwards, the resulting zeolite (500 mg) was introduced in reactor then suspended in hexane and stirred at 25 °C (±2 °C) under nitrogen.

Five hundred milligrams of HFAU(15) is added in a round bottomed flask to 50 mg of cholesterol (Aldrich, recrystallized, pure per GC) dissolved in 50 ml of hexane (HPLC grade). Periodically, aliquots (2 ml) are removed from the reaction mixture and centrifuged to separate the organic layer from the zeolite. The zeolite is then washed with chloroform and the combined organics are evaporated to dryness under nitrogen flux before analyses by GC and GC–MS.

The GC analysis of the transformation products and steroid standards were carried out on a Hewlett-Packard 6890 GC (split injector, 250 °C; Flame Ionisation Detector (FID), 300 °C) using a fused silica capillary column (SGE BPX 5%, 30 m × 0.25 mm i.d., 0.25 μm film thickness) and helium as carrier gas. The GC was temperature programmed from 60 to 300 °C at 5 °C min^{-1} (isothermal for 20 min final time).

The GC–MS analysis were carried out on a Trace GC Thermo Finnigan coupled to a Thermo Finnigan Automass (same analyses conditions). The MS was operated in the electron impact mode at 70 eV ion source energy and the ions separation was operated in a quadripolar filter.

Compounds were identified on the basis of their GC retention times and by comparison of mass spectra with those of literature, library data and spectra of authentic standards (commercial or synthesised in the laboratory). Unknown compounds were characterized by interpretation of the fragmentation pattern of their mass spectra. The relative concentrations of reaction products were estimated from ratios of the chromatographic peaks areas, what assume that the detection response is linear over the range of concentrations observed and that the response factors are similar for the different steroidal compounds.

After reaction, carbon content deposited on used zeolite was determined by calcination at 1293 K under helium and oxygen using a Thermoquest NA 2100 elementary analyser.

Fourier transform infrared (FT-IR) spectrum of used zeolites were obtained in KBr pellet using a Perkin-Elmer Spectrum 1000 spectrometer.

Furthermore, the used zeolite was recovered in order to analyse the compounds retained in the internal pores following the technique already described [18]: extraction through Soxhlet® by CH_2Cl_2 before dissolution of zeolite in HF solution and recovering the organic compounds in CH_2Cl_2. These compounds were analysed by GC–MS coupling in the same conditions that it was previously described for the analysis of reaction products. The experiment was performed three times with same results.

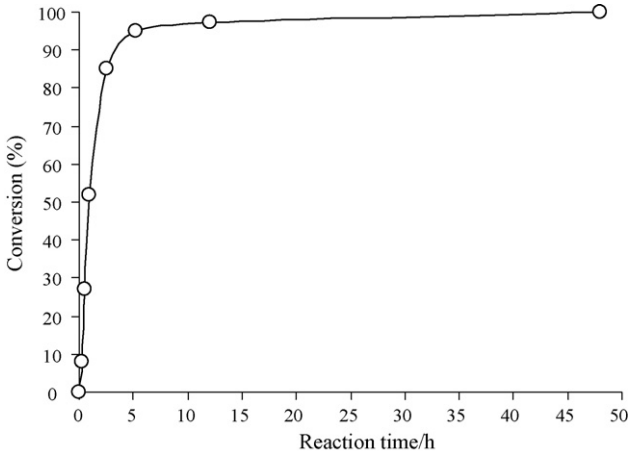


Fig. 2. Cholesterol conversion as a function of time over HFAU(15) at 25 °C.

3. Results and discussion

3.1. Activity

Zeolite is very active, even at 25 °C. Thus, after 15 min reaction, about 8% of reactant was transformed (Fig. 2). Moreover, about 50 and 95% of cholesterol were transformed after 1 and 5 h reaction, respectively. The activity of the catalyst, calculated for 15 min reaction, can be estimated to be equal to 1.35×10^{-4} mol h^{-1} g^{-1}. This initial activity can be related to the acidity of HFAU zeolite: about 327 μmol g^{-1} of Brönsted acid sites able to retain adsorbed pyridine at 150 °C (Table 1). However, the turn over frequency value (TOF) calculated as the number of cholesterol molecules transformed per hour and per Brönsted acid sites able to retain pyridine at 150 °C, is relatively weak because equal to 0.41 h^{-1}. Various reactions followed during 1 h were carried out with various zeolite content (125, 250 and 500 mg) and also with a smaller particle size (0.2–0.4 and 0.1–0.2 mm). Whatever the operating conditions, activities calculated for low conversion (2–10%) were close to $1.3–1.5 \times 10^{-4}$ mol sterol transformed h^{-1} g^{-1} catalyst.

3.2. Product distribution and coke analysis

Fig. 3 shows some examples of the GC evolution of cholesterol and reaction products as a function of reaction time. Table 2 gives the formula of the products formed in the reaction mixture and Table 3 their relative abundances during the reaction. All the products are formed after 24 h reaction (Table 2) and a complex mixture was analysed (see after 3 weeks, Fig. 3). No significant change can be observed in the distribution of the reaction products of cholesterol after three weeks of reaction (not presented) because of the zeolite deactivation.

The evolution of the yield of reaction products was followed in Fig. 4 for the first 12 h reaction. The first product initially formed is the cholesta-3,5-diene (**1**) rapidly followed by the formation of the cholesta-4,6-diene (**2**). These cholestadienes are known to be formed by dehydration of cholesterol [19] leading to the cholesta-3,5-diene (**1**) which is isomerised into cholesta-4,6-diene (**2**).

Table 2
Compounds and their first detection time (f.d.t.)

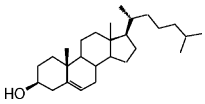
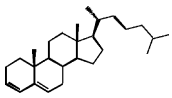
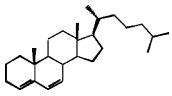
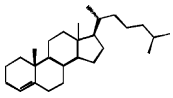
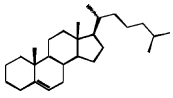
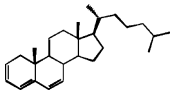
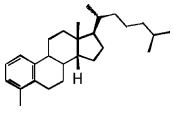
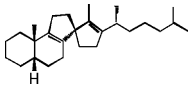
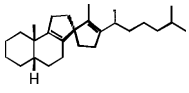
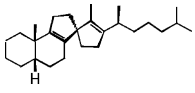
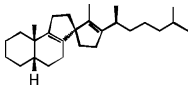
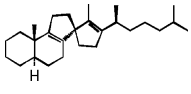
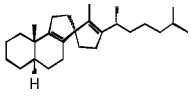
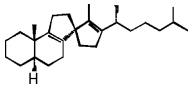
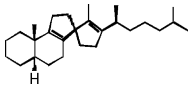
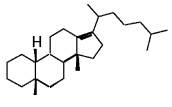
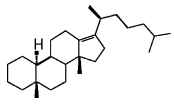
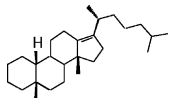
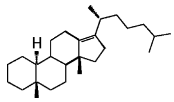
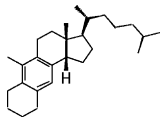
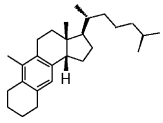
Compound		Structure	f.d.t. (h)
C	Cholest-5-ene-3β-ol		
1	Cholesta-3,5-diene		0.25
2	Cholesta-4,6-diene		0.25
4	Cholest-4-ene		1
5	Cholest-5-ene		1
6	Cholesta-2,4,6-triene		12
7	4-methyl-19-norcholesta-1,3,5(10)-triene		24
15a	Spiro-(14*R*)-(20*R*)-5β(H)-cholesta-8,13(17)-diene		24
15b	Spiro-(14*S*)-(20*R*)-5β(H)-cholesta-8,13(17)-diene		12
15c	Spiro-(14*S*)-(20*S*)-5β(H)-cholesta-8,13(17)-diene		24
15d	Spiro-(14*R*)-(20*S*)-5β(H)-cholesta-8,13(17)-diene		24
15e	Spiro-(14*R*)-(20*S*)-5α(H)-cholesta-8,13(17)-diene		24
15f	Spiro-(14*S*)-(20*R*)-5α(H)-cholesta-8,13(17)-diene		1
15g	Spiro-(14*R*)-(20*R*)-5α(H)-cholesta-8,13(17)-diene		1
15h	Spiro-(14*S*)-(20*S*)-5α(H)-cholesta-8,13(17)-diene		12
16a	Dimethyl-dinor-8α,9β,10β-cholest-13-(17)-ene(20*S*)		24

Table 2 (*Continued*)

Compound		Structure	f.d.t. (h)
16b	Dimethyl-dinor-8α,9β,10α-cholest-13-(17)-ene(20*S*)		24
16c	Dimethyl-dinor-8α,9β,10β-cholest-13-(17)-ene(20*R*)		24
16d	Dimethyl-dinor-8α,9β,10α-cholest-13-(17)-ene(20*R*)		12
17a	14α(H)-(10 → 6)-abeo-cholesta-5,7,9(10)-triene		24
17b	14β(H)-(10 → 6)-abeo-cholesta-5,7,9(10)-triene		24

Cholestadienes formed at relatively low conversion appear as primary products, thus, for 8% of cholesterol transformed, only cholestadienes were formed (Table 3) and the selectivity in cholestadienes (Compounds **1** and **2**) was equal to 100%. After what, the concentration of cholestadienes (especially Compound **1**) in the reaction mixture, decreases and these are transformed into other compounds (Fig. 4). These products are mainly spirocholestadienes, cholestenes, diacholestenes, cholestadienes and monoaromatics, spirocholestadiene (Compounds **15**) being the principal components formed after 120 h reaction (Table 3).

After the end of the reaction (3 weeks), zeolite was recovered and retained products on the zeolite were extracted by Soxhlet treatment with CH_2Cl_2. The carbon content initially close to 4.0 wt% after reaction decreases to 2.0 wt% after soxhlet extraction which means that 50% of compounds retained on zeolite can be extracted by this method. Fig. 5 shows the FT-IR spectrum of

Table 3
Relative concentrations (% of the total starting cholesterol, T: traces) of the most important (in abundance) products of cholesterol over the 528 h (3 weeks) of experiment

	Hours							
	0.25	1	2.5	12	24	48	120	528
Cholest-5-ene-3β-ol (C)	92.0	48.0	14.7	2.5	0.4	T		
Cholesta-3,5-diene (**1**)	7.0	43.2	66.8	62.7	54.4	37.3	22.4	8.0
Cholesta-4,6-diene (**2**)	0.7	7.3	15.2	21.0	18.9	13.2	7.9	2.7
Cholest-4-ene (**4**)		0.6	1.2	2.0	2.0	1.8	1.5	1.0
Cholest-5-ene (**5**)		0.2	0.4	0.7	0.9	0.9	0.8	0.7
Cholesta-2,4,6-triene (**6**)				T	T	T	T	T
4-methyl-19-norcholesta-1,3,5 (10)-triene (**7**)					0.7	0.9	1.2	2.0
Spiro-(14*R*)-(20*R*)-5β(H)-cholesta-8,13(17)-diene (**15a**)					T	T	T	T
Spiro-(14*S*)-(20*R*)-5β(H)-cholesta-8,13(17)-diene (**15b**)				1.0	2.4	4.4	5.6	5.9
Spiro-(14*S*)-(20*S*)-5β(H)-cholesta-8,13(17)-diene (**15c**)					0.6	1.9	3.4	5.5
Spiro-(14*R*)-(20*S*)-5β(H)-cholesta-8,13(17)-diene (**15d**)					T	T	T	T
Spiro-(14*R*)-(20*S*)-5α(H)-cholesta-8,13(17)-diene (**15e**)					0.1	0.6	1.3	2.2
Spiro-(14*S*)-(20*R*)-5α(H)-cholesta-8,13(17)-diene (**15f**)		0.3	1.0	6.1	11.1	16.2	19.0	17.6
Spiro-(14*R*)-(20*R*)-5α(H)-cholesta-8,13(17)-diene (**15g**)		0.3	0.5	0.6	0.7	0.9	1.5	2.4
Spiro-(14*S*)-(20*S*)-5α(H)-cholesta-8,13(17)-diene (**15h**)				0.7	1.8	4.1	7.0	11.2
Dimethyl-dinor-8α,9β,10β-cholest-13-(17)-ene(20*S*) (**16a**)					T	T	T	0.3
Dimethyl-dinor-8α,9β,10α-cholest-13-(17)-ene(20*S*) (**16b**)				0.5	0.9	1.3	1.9	3.9
Dimethyl-dinor-8α,9β,10β-cholest-13-(17)-ene(20*R*) (**16c**)					0.3	0.5	0.7	1.3
Dimethyl-dinor-8α,9β,10α-cholest-13-(17)-ene(20*R*) (**16d**)				0.9	1.8	3.4	5.3	9.2
14α(H)-(10 → 6)-abeo-cholesta-5,7,9(10)-triene (**17a**)					0.2	0.3	0.4	0.6
14β(H)-(10 → 6)-abeo-cholesta-5,7,9(10)-triene (**17b**)					0.3	0.8	1.2	1.9

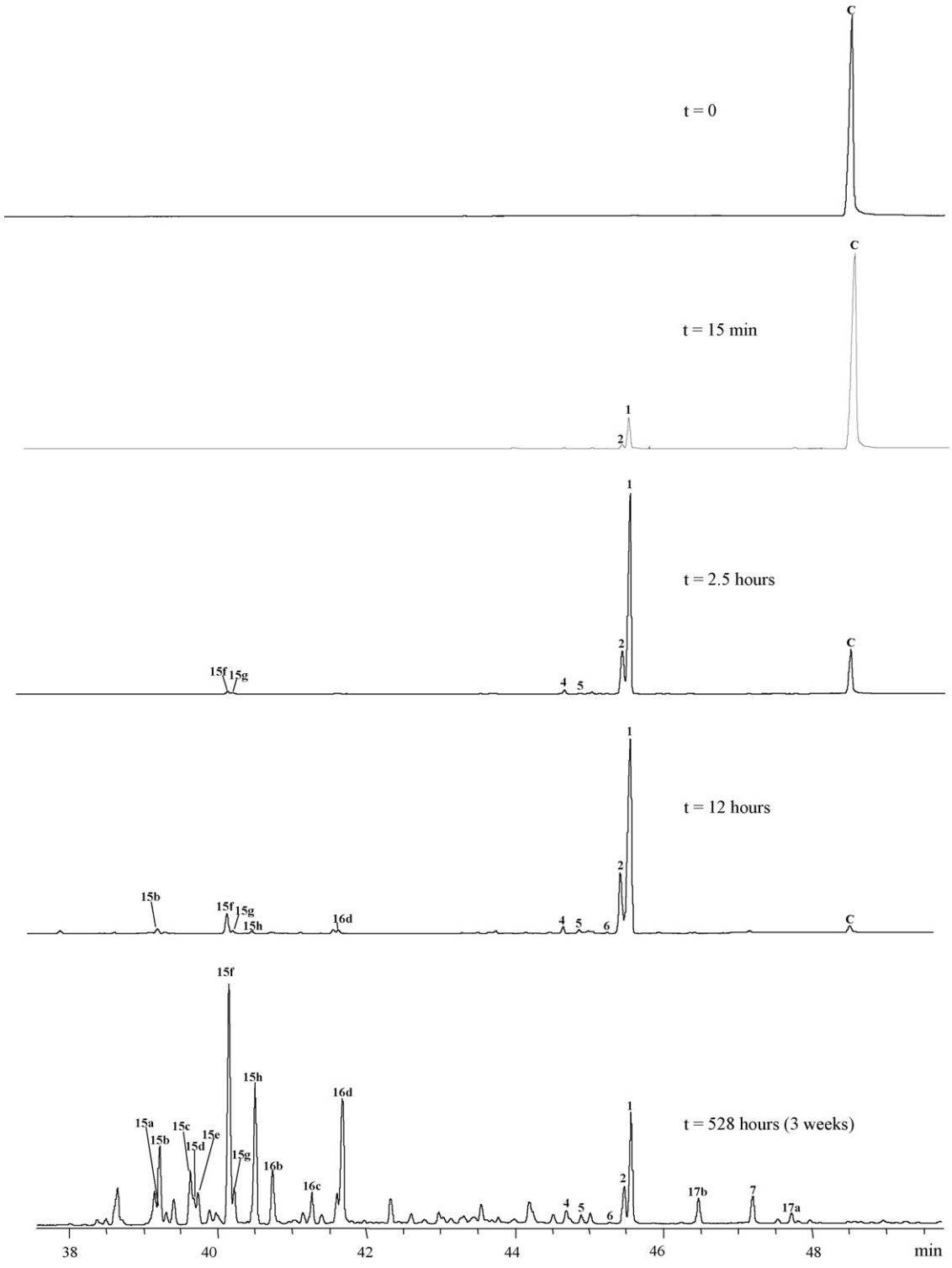


Fig. 3. GC of the products resulting to the transformation of cholesterol on HFAU(15) zeolite (see Table 2 for the numbered compounds).

these compounds which exhibited a broad bands at 1702 cm^{-1} (carbonyl) and strong bands centred at 2931, 2853, 1448, 1381, 1216 and 756 cm^{-1} which can be attributed to CH_3 and/or CH_2 groups. The FT-IR spectrum revealed also the presence of vinylic groups (band centred at 3014 and 1600–1700 cm^{-1}).

GC–MS analysis indicates the presence of oxygenated compounds (mono- and dioxygenated molecules), cholesta-3,5-dien-7-one, cholesta-4-en-3-one and cholesta-4,6-dien-3-one were also identified. Such ketones could be produced from dehydration of cholesterol. Besides, spirocholestadienes and diacholestenes were detected.

Catalyst was then treated by HF followed by CH_2Cl_2 extraction. The part recovered after HF treatment (50% of compounds) was constituted by a complex mixture of compounds of which a

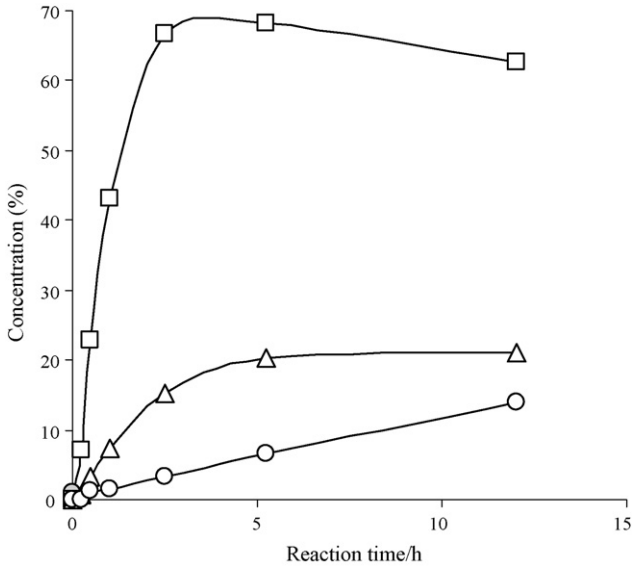


Fig. 4. Concentration of reactions products during the first 12 h of the experiment: (□) cholesta-3,5-diene, (△) cholesta-4,6-diene and (◯) others.

detailed analysis is difficult. Nevertheless, a selective detection in mass spectroscopy at m/z 253 suggests the presence of a great number of aromatic compounds. The presence of these compounds seems to indicate that part of reaction occurs in the inner pores of the zeolite. From these results, it is possible to estimate that the conversion of cholesterol (or these reaction products) into non-desorbed products "coke" was close to 40–45%, but also that "coke" molecules (average molecular weight of 400 g) occupy only 10% of the total cavities of HFAU zeolites.

3.3. Mechanism of formation of secondary products

3.3.1. Cholestenes (Compounds **4** and **5**)

Cholestenes are detected from 1 h reaction and are present all along the reaction in few amounts, they are cholest-4-ene (**4**) and cholest-5-ene (**5**). In absence of hydrogen, the generally accepted pathway suggests a proton transfer between two dienes to give cholest-5-enes (that can rapidly equilibrate with the Δ^4-isomer [20,21]) and cholastatriene who can evolve towards aromatic compounds who are retained on zeolite.

3.3.2. Diacholest-13(17)-enes (Compounds **16**)

Four compounds are identified as (20*R*)-, (20*S*)-10α(H) and (20*R*)-, (20*S*)-10β(H) epimers of diacholest-13(17)-ene (**16a**–**d**). They are present in relatively high quantities (more than 15% of the recovered products) at the end of the experiment (Table 3).

The quantity of these four diacholestenes increases with reaction time till the deactivation of the zeolite. **16d** and **16b** are obtained in higher relative abundance than the two others (Table 3). They are identified as (20*R*)-10α(H)-diacholest-13(17)-ene and (20*S*)-10α(H)-diacholest-13(17)-ene, respectively. **16c** and **16a** are identified as (20*R*)-10β(H)-diacholest-13(17)-ene and (20*S*)-10β(H)-diacholest-13(17)-ene. These four products are known to be issued from the backbone rearrangement of cholest-5-ene (**5**) and cholest-4-ene (**4**) [21]. The rearrangement occurs via a series of carbocation-alkene interconversions and gives rise initially, via a semi-diasterene intermediary, to diacholestene **16d** (the first of them, detectable in the medium after 5 h of reaction) which then undergoes isomerisation at C-20 (with increasing reaction time) giving the diacholestene **16b**. **16c** must be formed via the semi-diasterene intermediate, but in lower relative abundance than **16d**, and then undergoes isomerisation at C-20 giving the diacholestene **16a**.

3.3.3. Spiro-cholestadienes (Compounds **15**)

These products represent the most important compounds formed after 120 h of cholesterol reaction over HFAU(15).

The rearranged product **15f** appears after 1 h and was identified as (14*S*)-(20*R*)-5α(H)-12(13 → 14)-*abeo*-cholesta-8,13(17)-diene. This compound had already been detected in

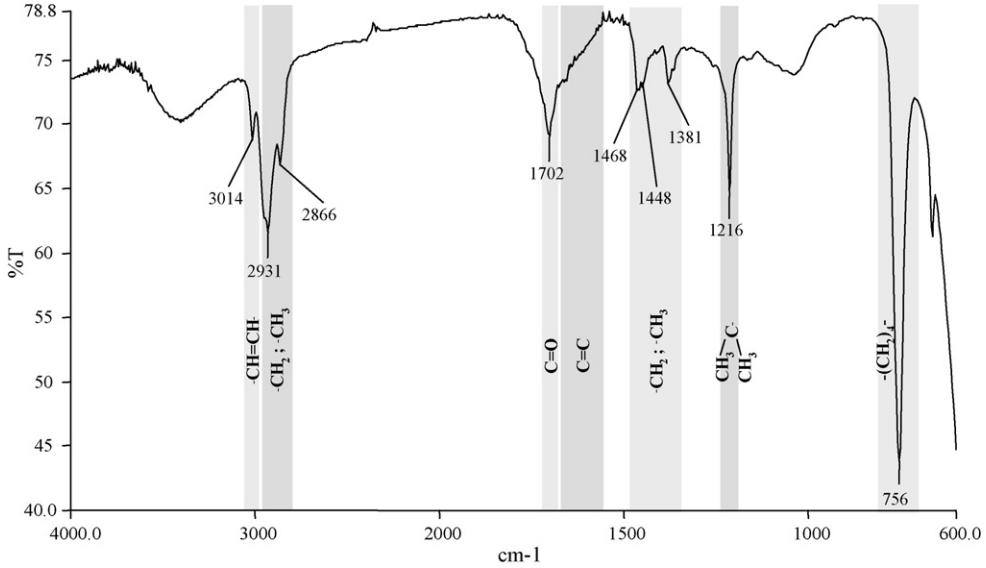


Fig. 5. FT-IR spectrum of compounds retained on zeolite and recovered after Soxhlet extraction with CH_2Cl_2.

studies of rearrangement products of cholesta-3,5-diene [22] or 5α(H)-cholest-8,14-diene [23] in the presence of *p*-TsOH in AcOH at 70 °C. With further reaction time (Table 3), eight isomers were detected (**15a–h**). They have been identified as (20*R*)-, (20*S*)-5β and (20*R*)-, (20*S*)-5α epimers of (14*S*)-12(13 → 14)-*abeo*-cholesta-8,13(17)-diene [22,23] and (20*R*)-, (20*S*)-5β and (20*R*)-, (20*S*)-5α epimers of (14*R*)-12(13 → 14)-*abeo*-cholesta-8,13(17)-diene. These eight cholestadienes are the major classe of by-products of cholesta-3,5-diene (**1**).

Spiro-cholestadiene **15f** and its isomers originate from the isomerisations undergone by cholesta-3,5-diene (**1**) and cholesta-4,6-diene (**2**) through pathways including cholestadienes as intermediates and via allylic cations by reversible protonation-deprotonation reactions. $\Delta^{8,14}$ steroids are known to be major by-products of $\Delta^{5,7}$ steroids under acidic conditions [24,25] and Liu et al. [23] has shown that cholesta-8,14-dienes give spiro-cholestadienes in the presence of *p*-TsOH in AcOH. On the other hand, cholesta-8,14-dienes, implicated as an intermediary, seems to react quickly in a irreversible way and were then detected only as traces.

The first two identified spiro-cholestadienes are the Compounds **15f** and **15g** (Table 3). The 5α(H) epimers of spiro-cholestadienes are preferentially formed, compared to the 5β(H) epimers, but also that C-14 isomerisation would be done very early and would be kinetically favoured. The preferential formation of the 5α(H) epimers can be explained by the greater reactivity of the 5α(H) epimers of cholesta-6,8(14)-diene [26].

With further reaction time, one observes the formation of spiro-cholestadienes **15e**, **15h**, **15b**, **15c**, **15a** and **15d**. After 2 weeks, the quantity of spiro-cholestadienes (**15**) in the medium stops to increase. The equilibrum between Compounds **15e** and **15g**, **15b** and **15c**, **15f** and **15h** (Fig. 6) corresponds to the equilibrium between the (20*R*) and (20*S*) forms of the three isomers. Isomers **15a** and **15d** are detected in small quantities and elute with other steroids, making difficult a precise follow-up.

Spiro-(14*S*)-(20*R*)-5α(H)-cholestadiene (**15f**) is the first to be formed. Next, it would undergo an isomerisation at C-14 to form the spiro-(14*R*)-(20*R*)-5α(H)-cholestadiene (**15g**) and then an epimerisation at C-20 to form the spiro-(14*S*)-(20*S*)-5α(H)-cholestadiene (**15h**). Spiro-(14R)-(20S)-5α(H)-cholestadiene (**15e**) could be issued from an isomerisation at C-14 on spiro-(14*S*)-(20*S*)-5α(H)-cholestadiene (**15h**) or at C-20 on spiro-(14*R*)-(20*R*)-5α(H)-cholestadiene (**15g**). Spiro-(14*S*)-(20*R*)-5β(H)-cholestadiene (**15b**) that would be issue from the 5β(H)-cholesta-6,8(14)-diene would be formed later than **15f** (this epimer being less reactive than the 5α(H)-cholesta-6,8(14)-diene). It would then undergo epimerisation at C-20 to form the spiro-(14*S*)-(20*S*)-5β(H)-cholestadiene (**15c**). Isomers **15a** and **15d** which would come, respectively, from a C-14 and C-20 isomerisation of **15b** compound are present only as traces. Nevertheless, these assumptions are based on the irreversibility of the formation of cholesta-6,8(14)-diene starting from cholesta-5,7-diene [27]. In the contrary case, spiro-cholestadiene **15f** could isomerise in **15b** and the **15h** in **15c**.

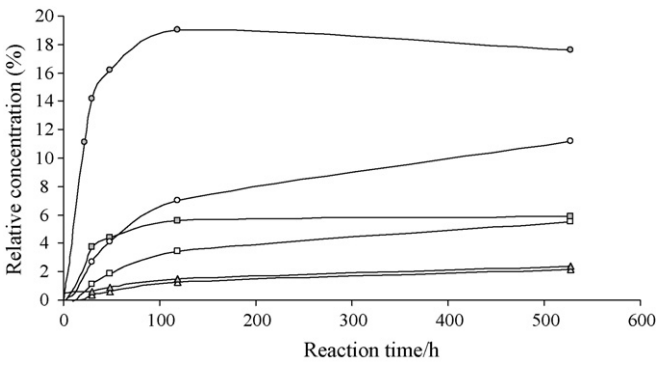


Fig. 6. Evolution of the quantities of spiro-cholestadienes during the reaction: (■) **15b**, (□) **15c**, (△) **15e**, (▲) **15f**, (●) **15g** and (◯) **15h**.

3.3.4. Rings A and B monoaromatic Compounds **17**

Rings A and B monoaromatic compounds are detected in the reactional medium after 24 h and their proportion within the medium increases slowly throughout the reaction to reach nearly 5% of the remained products at the end of the study.

Compounds **17b** and **17a** are identified on the basis of their mass spectrum as being, respectively, epimers 14β(H) and 14α(H) of 1(10 → 6)-*abeo*-cholesta-5,7,9(10)-triene (anthrasteroids). Compound **7** is identified as being 4-methyl-19-*nor*-cholesta-1,3,5(10)-triene.

Olgivie [28] has suggested that rings A and B monoaromatic compounds result from reactions of elimination and protonic rearrangements undergone, respectively, by cholesta-1,3,5-triene in the case of ring A components and cholesta-3,5,7-triene in the case of ring B ones. This assumption is confirmed by Schüpfer [22]. By carrying out an acidic treatment on cholest-3,5-diene (**1**), marked (with ^{13}C) at C-4 position, he obtains ring A product, marked in C-10 and ring B marked in equal quantities in C-1 and C-4. The reactional way leading to A-monoaromatic can pass by a tertiary carbocation at C-5 and this last can undergo a contraction of its cycle B to form the "spiro" intermediary (carbocation stabilized by resonance). The opening of the cycle B and the formation of the connection between C-9 carbon and marked carbon would lead then to A-monoaromatic (**7**). The way leading to B-monoaromatic compounds can also pass by a "spiro" intermediary with the contraction of cycle A. From the carbocation, two reactional ways can be possible (with equal probability), they can lead to the anthrasteroids **17** with the carbon marked at C-1 and C-4.

An other possible way of formation for the rings A and B monoaromatic compounds is the rearrangement of cholesta-2,4,6-triene (**6**). Such a rearrangement occur in the presence of *p*-toluenesulfonic acid (TsOH) in acetic acid (AcOH) at 70 °C leads to 4-methyl-19-*nor*-cholesta-1,3,5(10)-triene (**7**) and 1(10 → 6)-*abeo*-14β-cholesta-5,7,9(10)-triene (**17b**) [22]. As cholesta-2,4,6-triene (**6**) is detected in our experiment as traces among the compounds of transformation of cholesterol, it could be, as well others cholestatrienes, and such as cholesta-3,5,7-diene which are detected as components of coke and among retained compounds, key intermediaries during rearrangement leading to components **7**, **17a** and **17b**.

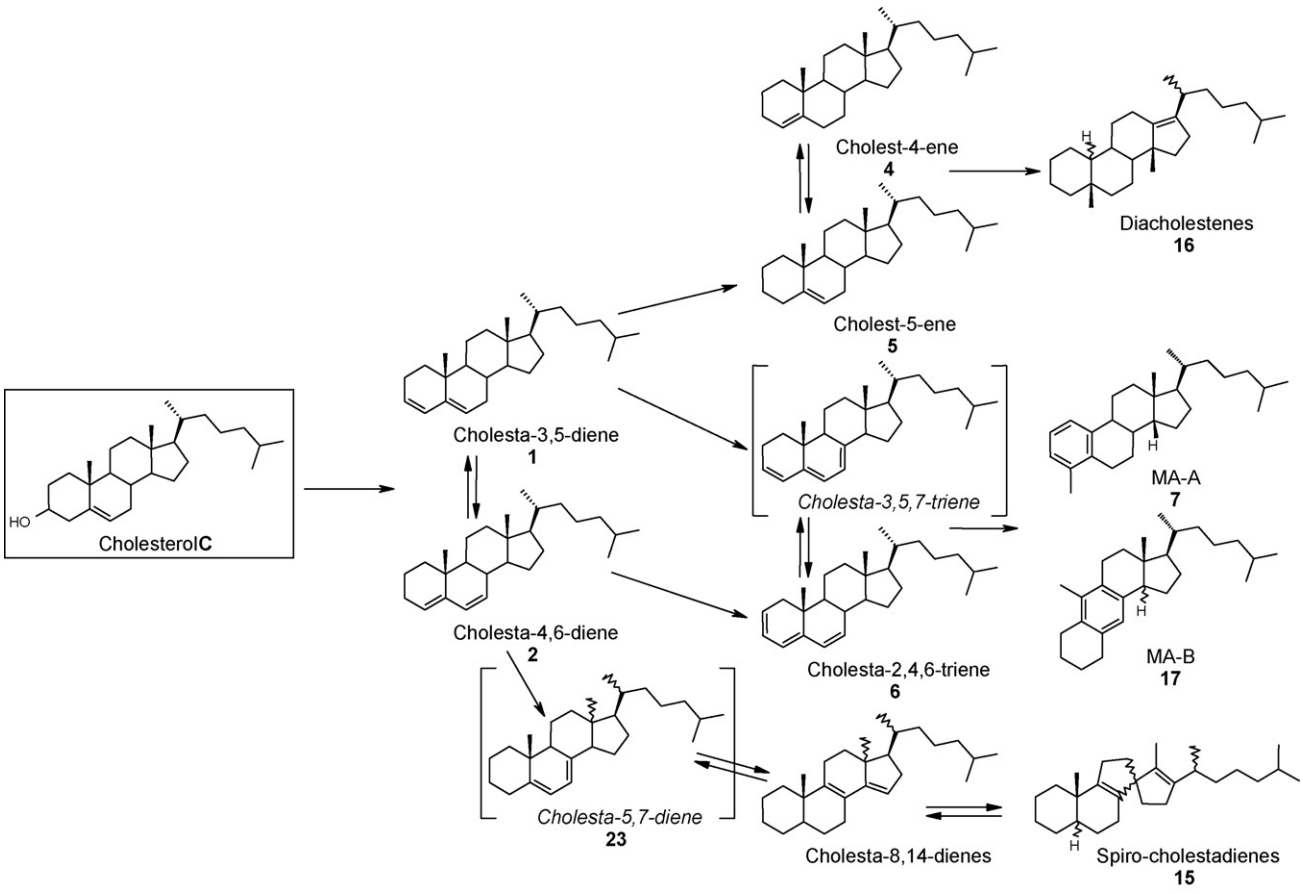


Fig. 7. Synthetic alteration scheme for cholesterol to its acid catalised products on zeolite HFAU(15): dehydration, reduction, backbone rearrangement, ring opening and aromatic compounds.

4. Conclusion

The transformation of cholesterol, a model molecule from the biomass, was followed at ambient temperature (25 °C) over an acidic zeolite catalyst (HFAU(15)). The objective of this work was not the production of fuel or intermediates products from cholesterol but the comprehension of the mode of degradation of this sterol on heterogeneous acid catalyst. HFAU zeolite was here well adapted for this study because acidity was just necessary to follow systematically the evolution of reaction products as the function of time.

Cholesterol is firsly and quickly dehydrated in contact at 25 °C with HFAU(15) zeolite. The processed products are either "free" in the reactional medium or retained by the mineral matrix. After 3 weeks reaction, the fraction not retained by zeolite represents approximately 60% of the formed compounds. This fraction consists in no oxygenated unsaturated steroids that, quickly undergo transformations under the catalytic effect of zeolite. A synthetic alteration scheme for cholesterol to its acid catalysed products is proposed in Fig. 7.

Thus, cholesta-3,5-diene, which is the only free product to be directly issue from cholesterol, isomerises quickly in cholesta-4,6-diene. Cholest-3,5-diene is then transformed into cholest-5-ene which isomerises into cholest-4-ene. These cholestenes undergo rearrangements to form four diacholest-13(17)-enes epimers in C-10 and C-20.

Cholestadienes undergo series of isomerisation leading to the formation of the eight cholesta-8,14-dienes (epimers in C-5, C-13 and C-20) which lead to the formation and the isomerisation of eight spiro-cholestadienes (epimers in C-5, C-14 and C-20). Cholestatriene, quickly formed starting from equilibrium between cholestadienes seems to be partly responsible for the formation of rings A and B monoaromatic.

Non-desorbed products called "coke" were constituted by complex mixture constituted by ketonic compounds, directly extracted by soxhlet treatment and certainly located in the cavities of zeolite close to the external surface of crystallite and aromatic compounds strongly adsorbed in the zeolite cavities.

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