

Production of aromatic compounds in the heavy naphtha and light cycle oil ranges: catalytic cracking of aromatics and C₁₀ naphthenic-aromatics

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Abstract

BACKGROUND: The conversions of bicyclic compounds, both a naphthenic-aromatic compound (tetralin) and an aromatic compound (naphthalene), as model reactants representative of the heavy gasoline and light cycle oil (LCO) cuts in fluid catalytic cracking (FCC), were studied to understand the formation of C₁₀–C₂₀ aromatic compounds in gasoline and middle distillates cuts, in view of their impact on the properties of the cuts. A commercial FCC catalyst was used in its fresh, hydrothermally de-aluminated and equilibrium forms, at 450 °C in a fluidized bed CREC Riser Simulator reactor in the 2–8 s reaction time range.

RESULTS: Products were C₁–C₁₄ hydrocarbons and coke. Based on the product distributions, reaction networks were proposed for both reactants. The reactions considered in the networks were hydrogen transfer, cracking, ring opening and contraction, alkylation and disproportionation.

CONCLUSION: The load of zeolite in the catalysts and their acidities have the strongest influences on reaction selectivities. In the case of tetralin, the prevalent reaction is hydrogen transfer, which becomes more important as the catalysts are less active, the hydrocarbons with highest yields being C₁₀ aromatics. Cracking reactions predominate in naphthalene conversion over all the catalysts, a fact which favors mono-aromatic C₉– hydrocarbons. These results can help in the design of new FCC catalysts with better selectivity control.

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Keywords: catalysis; zeolites; polycyclic aromatic hydrocarbons (PAHs); catalytic processes

INTRODUCTION

Environmental care is the main driving force for regulations about the composition of transportation fuels,^{1,2} a fact which impacts severely on the production of both gasoline and diesel fuels, thus inducing strong changes in refining operations. Fluid catalytic cracking (FCC), the catalytic cracking of hydrocarbons, is one of the most important and profitable contributors to both pools.³ In relation to diesel fuels, whose composition can be made up of various hydrocarbon streams in the refinery, FCC contributes with its middle distillate cuts [light cycle oil (LCO), 180–350 °C].⁴ Regulations impose lower concentrations of sulfur and aromatic hydrocarbons, aimed at controlling gas and particulates emissions, and producing a better fuel quality.⁵ These two issues are severe problems in LCO, whose composition, including high concentration of both sulfur and aromatic compounds, is conditioned by the feedstock, the catalyst and the process conditions.⁴

Technological options exist to improve the quality of the LCO cut, such as the saturation (hydrogenation) of aromatic compounds,⁶ but they are expensive. However, the versatility of the FCC to process very different hydrocarbon feedstocks offers the chance to improve both yield and composition of the LCO cut by either changing the operative regime⁷ or making use of new catalysts designed to produce less aromatics.^{8,9}

The most important component in FCC catalysts is the Y zeolite, which is supported on a matrix (either active or inactive). The particles also include fillers, binders and, possibly, a number of additives. The cyclic operation of the unit induces strong changes in the catalyst particles, from their fresh state to the equilibrium state, due to the loss of aluminium atoms in the crystalline framework which induces a reduction of the unit cell size (UCS) and the occurrence of extra-framework aluminium species. The properties of equilibrium catalysts are extremely different from those in fresh catalysts, and the changes mentioned have a strong impact on product distributions and yields.^{10,11}

At present, the commercial offer of catalysts includes a large number of choices, but most of them are produced under a custom-made approach.¹² Any effort to produce specific catalysts to decrease the selectivity to aromatic hydrocarbons in LCO requires knowing with high detail the mechanisms leading

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to these compounds. However, publications are scarce for compounds in the boiling point range of diesel fuels, most of the research being focused on alkyl aromatics in the C₇–C₉ boiling range.¹³

The conversion of tetralin and naphthalene as model compounds was studied at moderate temperature and short reaction times in a Riser Simulator laboratory reactor using a commercial catalyst which was steam de-aluminated to produce samples with different properties, to be compared with the equilibrium form. A reaction network focused on the production of aromatic compounds in the boiling range of naphtha and light LCO was proposed.

EXPERIMENTAL

A commercial FCC catalyst formulated to maximize the yield of LCO was used in its fresh (Cat-F) and equilibrium (Cat-E) forms and de-aluminated by 100% steaming at different severities in a fluidized bed quartz reactor at 788 °C and residence times of 1, 3 and 5 h (Table 1).¹⁴ De-aluminated samples were named Cat-1, Cat-3 and Cat-5, respectively.

Zeolite UCSs were determined following the ASTM D-3942-91 X-ray diffraction technique, using a Shimadzu XD-1 X-ray spectrometer (Shimadzu, Kyoto, Japan). The textural properties of catalyst were determined by N₂ isotherms at 77 K with a Quantachrome Automated Gas Sorption System Autosorb-1 (Quantachrome Instruments, Boynton Beach, USA). The total area was calculated from the Brunauer, Emmett and Teller (BET) method (0.05 < P/P⁰ < 0.3) and the micropore volume and the external area were calculated from the t-plot method (3.5 Å < t < 7.0 Å). The pore size distribution was calculated from the adsorption branch according to the Barrett, Joyner and Halenda (BJH) method¹⁵ and the zeolite content was determined from the micropore area according to the Johnson method.¹⁶ The content of rare earths was determined by the inductively coupled plasma (ICP) method, using a Perkin Elmer Optical Emission Spectrometer OPTIMA 2100 DV (Perkin Elmer, Waltham, USA).

The nature, the amount and strength of acidic sites in the different zeolites were determined by means of the Fourier transform infrared (FTIR) analysis of adsorbed pyridine (99.5%; Merck, Darmstadt, Germany) as a probe molecule in a Shimadzu FTIR Prestige-21 equipment. Approximately 100 mg of the zeolite were pressed at 1 ton cm⁻² in order to produce self-supporting wafers with density 440 g m⁻², which were then placed into a cell with CaF₂ windows. Samples were initially degassed at 450 °C during 2 h and a background spectrum was collected at room temperature. Pyridine adsorption was performed at room temperature

and after successive desorptions at 150, 300 and 400 °C, spectra were recorded at room temperature with a resolution of 4 cm⁻¹ at a pressure of 10⁻⁴ Torr. The amounts of Brønsted and Lewis acid sites were calculated from the integrated absorbance of the bands at 1545 cm⁻¹ and 1450–1460 cm⁻¹, respectively, by means of the integrated molar extinction coefficients, which are considered independent of the catalyst and site strength.^{17,18}

The experiments of conversion of model reactants were performed in a CREC Riser Simulator laboratory reactor,¹⁹ designed to simulate FCC process conditions. The reactor has a turbine on top of a chamber that holds the catalyst bed between two porous metal plates. The turbine rotates at 7500 rpm, inducing a low pressure area in the upper central zone in the reactor that makes gases circulate in the upwards direction through the chamber, thus fluidizing the catalyst bed. When the reactor is at the desired experimental conditions, the liquid reactant is fed with a syringe through an injection port and vaporizes instantly, thus setting the initial reaction time. After the desired reaction time is reached, the gaseous mixture is evacuated immediately and products can be sent to analysis. Additional descriptive details can be found in Pasamonti *et al.*,²⁰ for example.

The reaction conditions were: temperature, 450 °C, catalyst to reactant ratio of 1.12, and reaction times between 2 and 8 s. The mass of catalyst was 0.2 g in all the cases. Experiments of thermal cracking (no catalyst was used) were performed at 450 °C and 8 s reaction time.

1,2,3,4-Tetrahydronaphthalene (tetralin, C₁₀H₁₂, ≥ 99%; Sigma–Aldrich) and naphthalene (C₁₀H₈, ≥ 99%, Merck) were used as model reactants. Naphthalene, which is solid at room temperature, was dissolved in benzene, in turn an essentially inert solvent under the reaction conditions, at 25 wt%.

The reaction products were analyzed by on-line standard capillary gas chromatography, using a 30 m length, 250 mm diameter and 0.25 mm film thickness, non-polar, dimethylpolysiloxane column. Product identification was performed with the help of standards and gas chromatography–mass spectrometry (GC–MS) analysis. The coke content was assessed by means of a method with temperature-programmed oxidation and further methanation.²¹ The mass balances in the experiments (recoveries) closed to more than 95%.

RESULTS AND DISCUSSION

Reactivity of the solvent

The conversion of benzene (no catalyst) was lower than 0.02% at 8 s reaction time, a fact which is consistent with reports by

Table 1. Properties of the catalysts used

Catalyst	Zeolite				Specific surface area (m ² g ⁻¹)		Pore volume (cc g ⁻¹)		Average mesopore diameter (nm)	Acidity (μmol Py g ⁻¹)					
	UCS (nm)	Load (wt%)	Si/Al	RE Content (wt%)	Matrix	Total	Micropore	Total		Bronsted (1545 cm ⁻¹)			Lewis (1450–1460 cm ⁻¹)		
										150 °C	300 °C	400 °C	150 °C	300 °C	400 °C
Cat-F	2.456	22.00	3.50	0.94	92	243	0.074	0.206	8.45	128.5	102.1	76.3	118.1	42.4	36.9
Cat-1	2.437	18.07	8.26	0.80	72	191	0.059	0.209	10.14	14.6	8.9	8.3	16.7	12.9	11.6
Cat-3	2.434	17.71	10.11	0.94	64	181	0.057	0.206	10.73	12.0	11.6	8.9	23.4	13.4	11.2
Cat-5	2.432	17.04	11.82	1.17	62	173	0.060	0.205	10.77	13.3	10.5	5.0	25.2	17.7	9.8
Cat-E	2.430	9.83	14.15	0.70	102	162	0.029	0.229	8.92	5.0	5.1	5.0	13.6	11.0	10.9

Moldoveanu,²² who pointed out a remarkable thermal stability up to 1000 °C. The catalytic conversions on catalysts Cat-F and Cat-E were lower than 0.36% at the longest reaction time of 8 s, with coke being the most important product. These results show that the contribution from benzene to the reaction products in the experiments with naphthalene can be disregarded.

Thermal cracking

The thermal cracking of tetralin and naphthalene produced conversions of 5.46% and 4.55%, respectively. The lower conversion of naphthalene, which has a higher degree of unsaturation (H/C = 0.8), reflected its higher thermal stability.²² The saturated ring in the molecule of tetralin reduces its unsaturation (H/C = 1.2), and makes it possible to form naphthalene,²² which was observed as the main product.

Catalyst properties

It can be seen in Table 1 that the majority of the properties of the fresh catalyst were modified after the hydrothermal treatment; in effect, the de-alumination causes the loss of aluminium atoms from the crystalline zeolite network due to the high temperature hydrolysis of the Si—O—Al bonds.²³ As a consequence, the UCS of the zeolite crystals decreased due to the higher Si content in the zeolite²⁴ and the Si/Al relationship changed, increasing steadily with steaming time. In this way, the sample which was de-aluminated during 5 h showed an UCS close to that of the equilibrium catalyst.

In this type of catalyst, micropores are contributed by the zeolite component (pore opening of Y zeolite 0.74 nm) and mesopores by the matrix and binder components,^{25,26} but vacancies in the zeolite framework due to de-alumination can produce breaks or even partial collapse of the crystalline material.²⁴ The partial collapse of the zeolite is also reflected as the loss of crystalline material, with the content decreasing steadily from the fresh to the equilibrium catalyst through the steamed samples, and also in the loss of acidity.^{23,27} This is consistent with observations from Matharu *et al.*,²⁸ who reported both micro- and mesoporosity in a hydrothermally treated Y zeolite, the mesopore volume increasing according to the severity of the treatment. Then, the occurrence of new pores after de-alumination, both in the Y zeolite and the matrix, could be manifested in the increasing average mesopore size and the decreasing total specific surface area of the catalysts (Table 1), as also observed by Salman *et al.*²⁹

The total acidity, as expressed by the pyridine FTIR spectra after desorption at 150 °C, decreased significantly from the fresh catalyst to the de-aluminated samples; moreover, it should be noted that the amount of acid sites in the de-aluminated catalysts does not differ significantly (Table 1). As it will be discussed later, particular attention will be given to Brønsted acidity in view of its mechanistic importance.

Figure 1 shows the conversion profiles of tetralin and naphthalene over the different catalysts, which are increasing in all the cases, though steeper with tetralin. It can be seen that in both cases catalyst Cat-F was the most active and catalyst Cat-E was the less active, with the de-aluminated samples showing intermediate conversions. This shows that catalyst activity is associated to zeolite load and acidity. Results in Fig. 1 also show that naphthalene is less reactive than tetralin. The unsaturated benzene rings, which are hardly reactive, in the molecule of naphthalene could be the reason for this observation.

Reaction pathways

Initial steps of reactions

Both tetralin and naphthalene molecules contain unsaturated benzene rings, which are a rich source of electrons (nucleophilic).³⁰ Then, the set of reactions on these reactants can be initiated through the electrophilic attack of catalyst surface protons and a resonant benzylic carbocation would be then formed, which has a stability similar to that of a secondary carbocation.³¹ This initial step has also been postulated for the reaction of alkylated benzenes such as isobutyl benzene³² or naphthenic-aromatic compounds such as 9,10-dihydrophenanthrene,³³ or even for the formation of coke from benzene.³⁴

In the case of tetralin, then, it is expected that a carbocation is formed by the protonation of the aromatic ring; Mostad *et al.* suggested that most likely the species is 1,2,3,4,9,10-hexahydronaphthalene,³⁵ with a tertiary carbocation formed by the positive charge located at position 9, as similarly proposed for the initial steps in the conversion of decalin over these catalysts.³⁶ In this sense, the resonating ability of this cation is assumed by Sato *et al.* in the example of tetralin hydrocracking over zeolite catalysts at 350 °C.³⁷ Moreover, either a tertiary carbocation with the charge at position 9 or secondary cations on the saturated ring, keeping the benzene ring unaltered, were suggested by Corma *et al.*³⁸ In this sense, Townsend and Abbot identified minor amounts of hydrogen in the conversion of tetralin over Y zeolite,³⁹ which could be the evidence of the formation of species with secondary cations on the saturated ring which release hydrogen into the medium.

In the case of naphthalene the reaction initiates through the formation of a benzylic carbocation. Park *et al.* suggested two initial steps in the hydrogenation of naphthalene over Pt/Al—MCM-41: the formation of a benzylic carbocation on the protonic acidic sites and the production of tetralin with the addition of hydrogen on the metallic sites.⁴⁰ The formation of the benzylic carbocation was also suggested by Guerzoni and Abbot in cracking 1-methylnaphthalene over HY zeolite.⁴¹ However, the formation of the secondary 1,2-dihydronaphthalene cation, which is the most stable among six possible cations cannot be disregarded,³⁰ since the full stability of a benzene ring would be maintained, as suggested in reactions of electrophilic substitution of polyaromatic compounds.³⁰ In this sense, Deward stated that in the comparison of the protonation of benzene and naphthalene,⁴² the latter shows a more basic character and is preferably protonated at the alpha position (carbon 1), the secondary carbocation being formed on carbon 2.

Reaction products

As shown by the experiments, the complex mixture of C₁–C₁₄ hydrocarbon products, including linear olefins and paraffins and cyclic naphthenics, naphthenic-aromatics and alkylated mono- and di-aromatic compounds, would then be the result of a set of mono-molecular or bi-molecular reactions starting on the initial either benzylic or secondary carbocations, starting from molecules such as tetralin and naphthalene. It is to be noted that the yields of coke in both cases is significant.

Considering the starting C₁₀ model reactants, the clearly identified reaction products and the observed yields (Table 2), the reactions in the network can be recognized as those of cracking (Cr), leading to products with a smaller number of carbon atoms per molecule (C₉); direct hydrogen transfer (HT), leading to hydrocarbons which maintain the bicyclic structure (C₁₀); ring opening (RO),

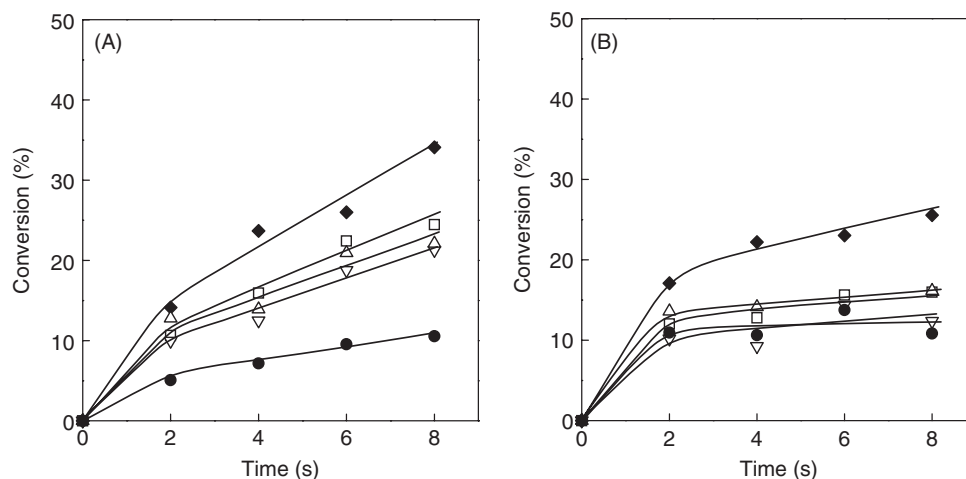


Figure 1. Conversion of model reactants as a function of reaction time: (A) tetralin, (B) naphthalene. Symbols: (◆) Cat-F, (□) Cat-1, (▽) Cat-3, (△) Cat-5, (●) Cat-E.

which can be considered as a step to the formation of light hydrocarbons and which can initially produce C_{10} compounds (alkylbenzenes), as proposed in the mechanism of the conversion of decalin;³⁶ ring contraction (RC), whose products are characterized by compounds including cycles with five members in their structure; and alkylation–disproportionation (A–D), producing hydrocarbons with eleven or more carbon atoms per molecule (C_{11+}).

These definitions do not imply a sequential order nor exclude other possible reactions, but they are an attempt to show the most important facts in the conversion of tetralin and naphthalene as the consequence of catalyst properties and reaction conditions, and which could be considered applicable to compounds with similar structures present in FCC feedstocks.

Based on the previous definitions, it can be identified in the case of tetralin that decalin and naphthalene are products from hydrogen transfer reactions, that ring opening reactions produce alkylated benzenes such as *n*-butylbenzene, that methyl indane is a product representative of ring contraction reactions, and that products such as methyltetralin and methylnaphthalene are representative of alkylation and disproportionation reactions. Also considering evidence from other authors about the hydrocracking of tetralin over acidic and bifunctional catalysts,^{35,37–39} a reaction mechanism on the acidic sites can be proposed (Scheme 1).

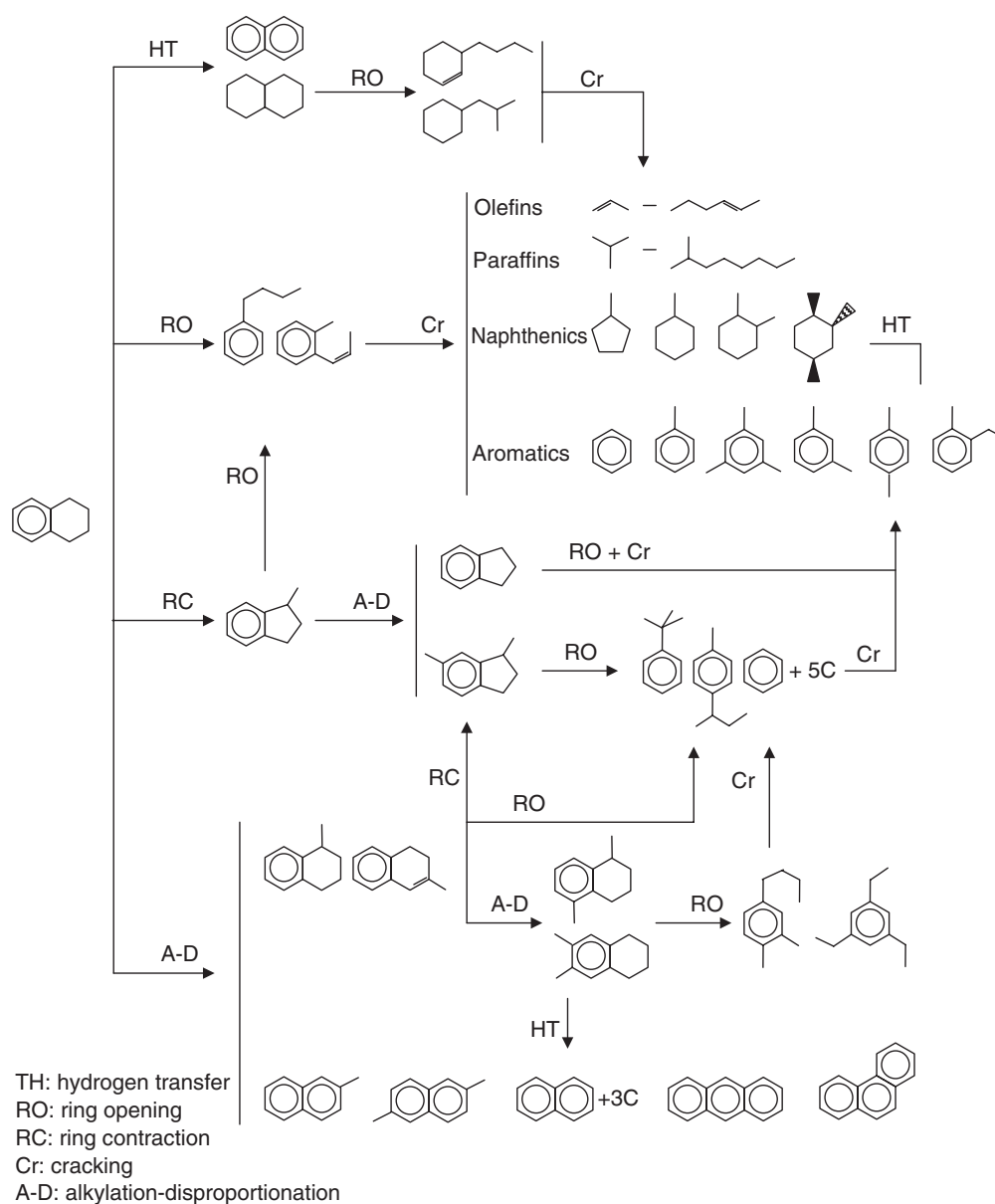
When naphthalene is the reactant, tetralin and methylnaphthalene are examples of the products of the hydrogen transfer and alkylation–disproportionation reactions, respectively. Even though ring opening products such as C_{10} alkylbenzene compounds were not specifically observed, the occurrence of light C_{9-} compounds could only be justified if ring opening products are considered as intermediate. This was proposed for the conversion mechanism of decalin.³⁶ These observations, in addition to others from studies about the hydrogenation and ring opening of naphthalene on bifunctional catalysts^{40,43,44} and cracking and hydrogenation of 1-methylnaphthalene,^{41,45} back the reaction pathways on the acidic sites, as shown in Scheme 2.

An important reaction in both cases is cracking, as represented by C_{9-} products (Table 2). It must be noticed in both proposed conversion pathways that cracking would be consecutive to ring opening of the reactants. Moreover, those which are initial reactions also occur in a sequential mode in the global model. For example, in the conversion of tetralin, hydrogen transfer reactions occur on the naphthenic products from cracking,

Table 2. Product yields (wt%) in tetralin and naphthalene conversion

Product	Tetralin	Naphthalene
$C_1 - C_2$	0.038	0.044
C_3	0.703	0.077
C_4 Olefins	0.044	0.008
C_4 Paraffins	1.006	0.035
C_5 Paraffins	0.374	–
Cyclopentane	0.031	–
C_6 Paraffins	0.116	–
C_6 Naphthenics	0.175	–
Benzene	2.037	11.644
Methylcyclohexene	0.004	–
C_7 Paraffins	0.025	–
C_7 Naphthenics	0.134	–
Toluene	1.283	0.887
C_8 Paraffins	0.017	–
C_8 Naphthenics	0.028	0.005
C_8 Aromatics	0.821	0.459
C_9 Paraffins	0.008	0.010
C_9 Aromatics	0.357	0.051
Indane	0.355	0.007
Tetralin	72.914	0.005
Isobutylcyclohexane	0.007	–
Decalin	0.197	–
3-Butylcyclohexene	0.004	–
C_{10} Aromatics	1.252	–
Naphthalene	11.592	77.802
(<i>E</i>)-(1-Methyl-1-propenyl)benzene	0.003	–
Methylindane	0.541	–
C_{11} Aromatics	0.107	–
Methylnaphthalene	0.555	0.022
Dimethylindane	0.219	–
Methyltetralin	0.044	0.158
C_{12}^+ Aromatics	0.243	0.012
C_{12}^+ Naphthenic aromatics	0.128	–
Coke	4.469	8.774

The catalyst was Cat-F and the reaction time was 4 s.



Scheme 1. Proposed reaction pathways: conversion of tetralin.

leading to aromatic products with nine or less carbon atoms per molecule (Scheme 1). A fact observed with both reactants (Schemes 1 and 2) is that bicyclic aromatics with 11 or more carbon atoms per molecule are formed from naphthenic-aromatic compounds.

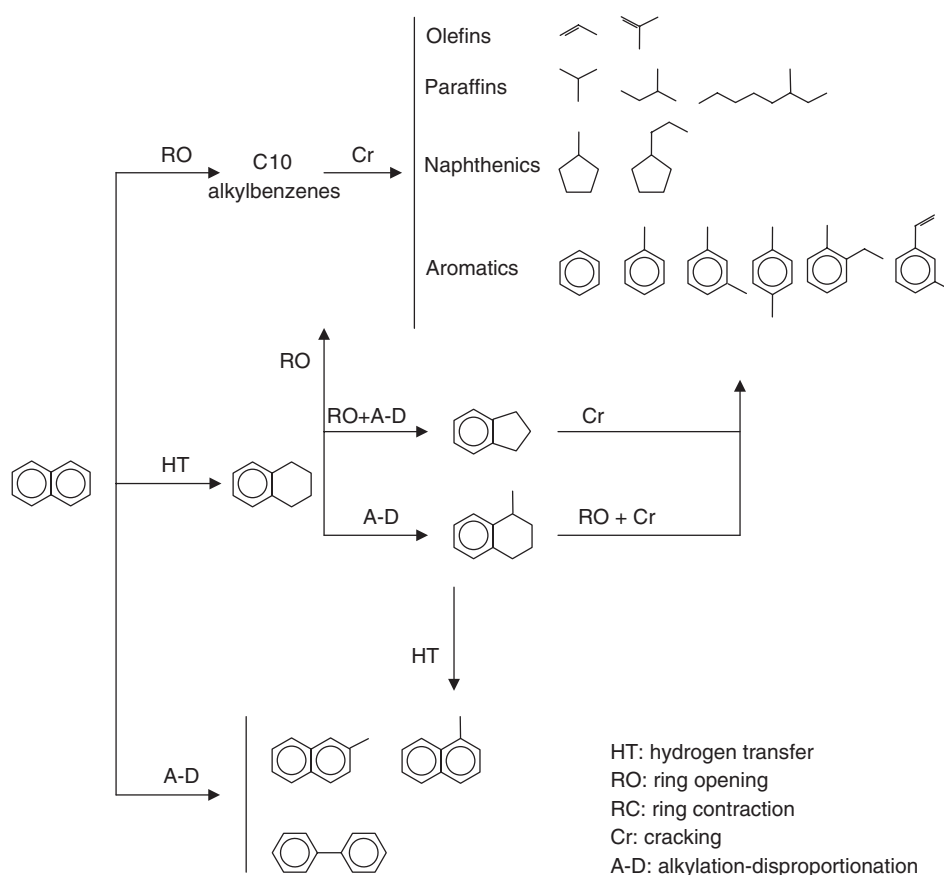
Reaction magnitudes

The comparison of the hydrocarbon yields as a function of conversion in each of the catalysts, for each of the reactions considered, allows defining rankings of magnitudes. Table 3 shows the reaction yields at approximately 10% conversion of the model reactants for the example catalysts Cat-F, Cat-3 and Cat-E, where it can be seen that in the conversion of tetralin over catalyst Cat-F, the order is $HT > Cr > RO \approx RC \approx A-D$. However, these differences become more significant in the cases of the de-aluminated catalysts, where hydrogen transfer is more important ($HT \gg Cr > RO \approx RC \approx A-D$) and, in the equilibrium catalyst Cat-E, this is even more pronounced, with a significant decrease of cracking products (HT

$\gg \gg Cr \approx RO \approx RC \approx A-D$). However, in the conversion of naphthalene over all the catalysts, the ranking of importance of the reactions was $Cr \gg \gg HT \approx A-D$ (refer to Table 3).

Table 3. Reaction yields (wt%) at approximately 10% conversion of tetralin and naphthalene

Reaction	Tetralin			Naphthalene		
	Cat-F	Cat-3	Cat-E	Cat-F	Cat-3	Cat-E
Hydrogen transfer	5.20	5.83	7.28	0.13	0.19	0.23
Cracking	3.47	2.00	0.57	7.00	5.72	9.72
Ring opening	0.50	0.82	0.99	0.00	0.00	0.00
Ring contraction	0.40	0.69	0.69	0.00	0.00	0.00
Alkylation-disproportionation	0.25	0.43	0.45	0.01	0.01	0.01



Scheme 2. Proposed reaction pathways: conversion of naphthalene.

The different behaviors of tetralin and naphthalene over these acidic catalysts without an external source of hydrogen clearly show that the molecule structures impact on the prevalence of the various reactions. In this way, naphthalene, which is completely aromatic, produces essentially benzene and coke while, in contrast, hydrogen transfer reactions leading to naphthalene, and coke, prevail with naphthenic-aromatic tetralin. It is to be expected in the case of tetralin that decalin, which is more reactive,^{35,46} would also be formed. Also, ring opening and contraction and cracking reactions may be competitive, according to the observed products.

The influence of de-alumination on the reactions can be analyzed in view of the different yields; results are shown for tetralin in Fig. 2 and for naphthalene in Fig. 3.

The yield curves of cracking and hydrogen transfer reactions in the case of tetralin show a primary character (Fig. 2A and B), while those of ring opening, ring contraction and show a secondary character (Fig. 2C and D). It can be seen in Fig. 2A that the yield of cracking products decreases as long as the catalysts are less active, following their lower zeolite content and acidity, as shown in Table 1. On the contrary, the other reactions have an opposite behavior, increasing their yields.

In comparison with the fresh catalyst, the lower amount of acidity of the de-aluminated and equilibrium catalysts, which, however, could have stronger acid strength, could favour some monomolecular reactions such as ring opening (which is an intermediate step to light cracking products) and ring contraction, thus making their yields more important than in the fresh catalyst, as observed in Fig. 2C and D. Note that the proportion of acidic sites

with higher acid strength (desorption temperature 400 °C, Table 1) increases from the fresh to the de-aluminated to the equilibrium catalyst.

It is to be expected that lower catalyst acidity would impact negatively on bimolecular reactions such as hydrogen transfer and alkylation–disproportionation. However, it can be seen that the yield of products from hydrogen transfer increases slightly when the acidity is lower (Fig. 2B), probably because the loss of acidic sites in the de-aluminated and equilibrium catalysts is not enough to impede these reactions, at least in the range of unit cell sizes considered (Table 1). Finally, the very low yield of alkylation–disproportionation reactions (results not shown) does not permit a clear analysis of the impact of the catalyst properties.

It can be observed in Fig. 3 that apparently the catalyst de-alumination process does not impact on the cracking of a totally aromatic molecule such as naphthalene. The slightly higher yield of cracking products of catalyst E-cat could be the consequence of a stronger acid strength.

Aromatic hydrocarbons

According to the type of hydrocarbons produced – olefins, paraffins, naphthenics and aromatics – it can be seen that aromatics were predominant in the conversion of tetralin over all the catalysts (Fig. 4), with the occurrence of an aromatic ring in the molecule being surely the main reason for conserving this character in the products. Besides this, the yields of olefins and saturated hydrocarbon products (C₉– paraffins and naphthenics) decrease as long as the catalysts are less active (Fig. 4A and B), with a behavior similar to that of cracking reactions (Fig. 2A). The yields

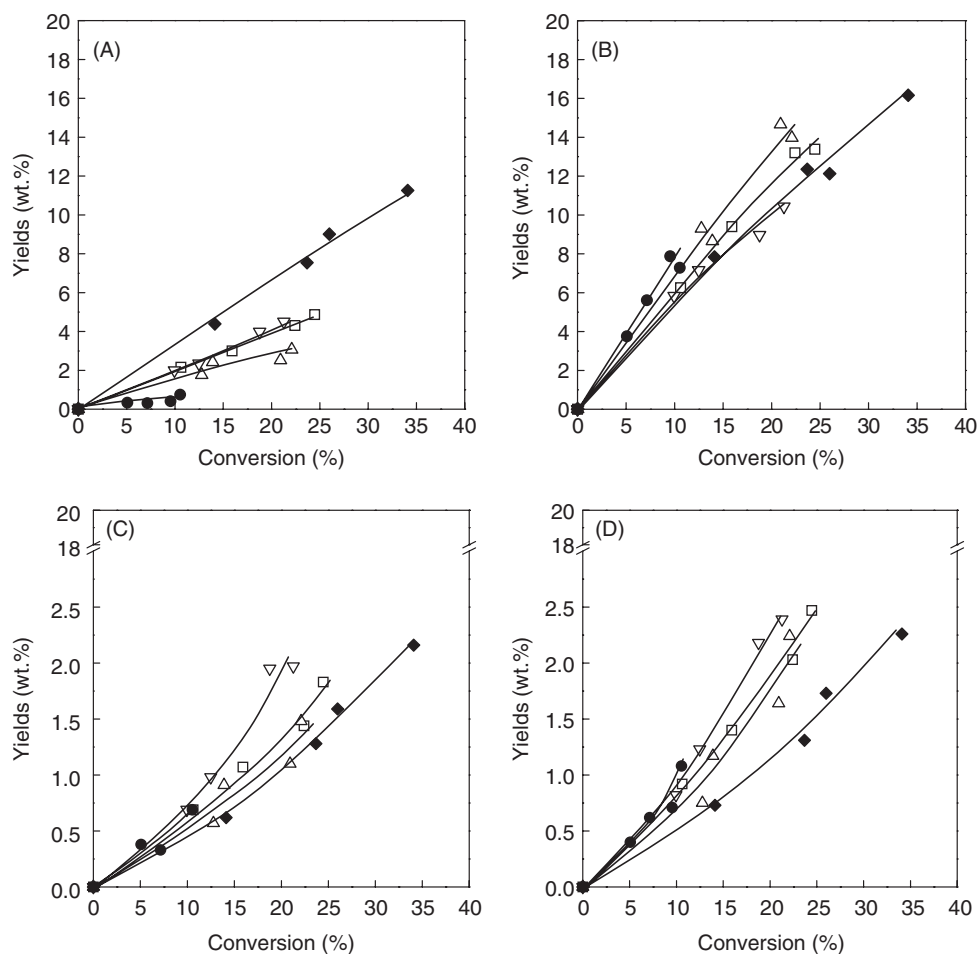


Figure 2. Yield curves for the different reactions of tetralin: (A) cracking, (B) hydrogen transfer, (C) ring contraction, (D) ring opening. Symbols as in Fig. 1.

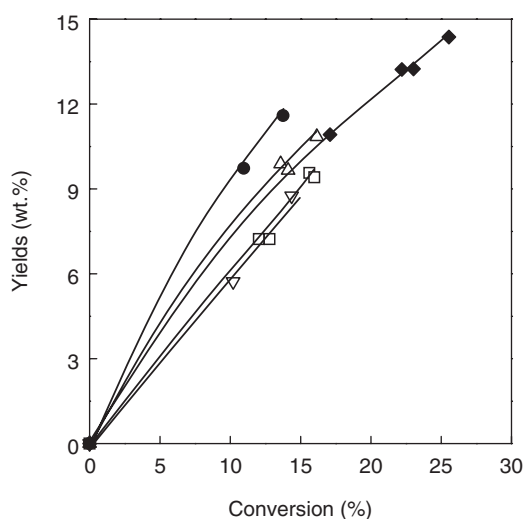


Figure 3. Product yields of cracking reactions of naphthalene. Symbols as in Fig. 1.

of aromatic hydrocarbons are very similar for all the catalysts (Fig. 4C).

The results shown indicate that the loss of crystalline material and catalyst acidity is not enough to impede the formation of aromatic hydrocarbons. This is more obvious in the de-aluminated

and equilibrium catalysts, where the yields of products from cracking reactions are even lower.

If aromatic hydrocarbons are classified according to the number of carbon atoms per molecule, then light C₆–C₉, intermediate C₁₀ and heavy C₁₁₊ groups can be defined, and it can be seen that the formation of intermediate aromatic compounds with the same number of carbon atoms per molecules as the reactant is highly favored (Fig. 5). This fact could be justified based on the prevalence of hydrogen transfer reactions over all the catalysts (Fig. 2B), which mainly produce naphthalene. If the yields over the various catalysts are compared, it can be seen that the yield curve of light C₉–aromatics (benzene, toluene, xylenes, ethylbenzenes and C₉ aromatics, see Fig. 5A) rule the behavior of cracking reactions shown in Fig. 2A, and that intermediate C₁₀ aromatics (Fig. 5B), the products of direct hydrogen transfer, control the behavior of the hydrogen transfer reactions shown in Fig. 2B. Besides naphthalene, the group includes mono-aromatic compounds which are the consequence of ring opening and contraction reactions of tetralin, such as butylbenzenes and methyl indane, respectively. Heavier aromatics, C₁₁₊, include methylnaphthalene and dimethyltetralin-type compounds from alkylation and disproportionation reactions.

The formation of di-aromatic compounds (particularly naphthalene) is favored from tetralin, due to the occurrence of a benzenic ring in the starting molecule and the strong impact of hydrogen transfer reactions on compounds which contain a saturated cycle on their structure.

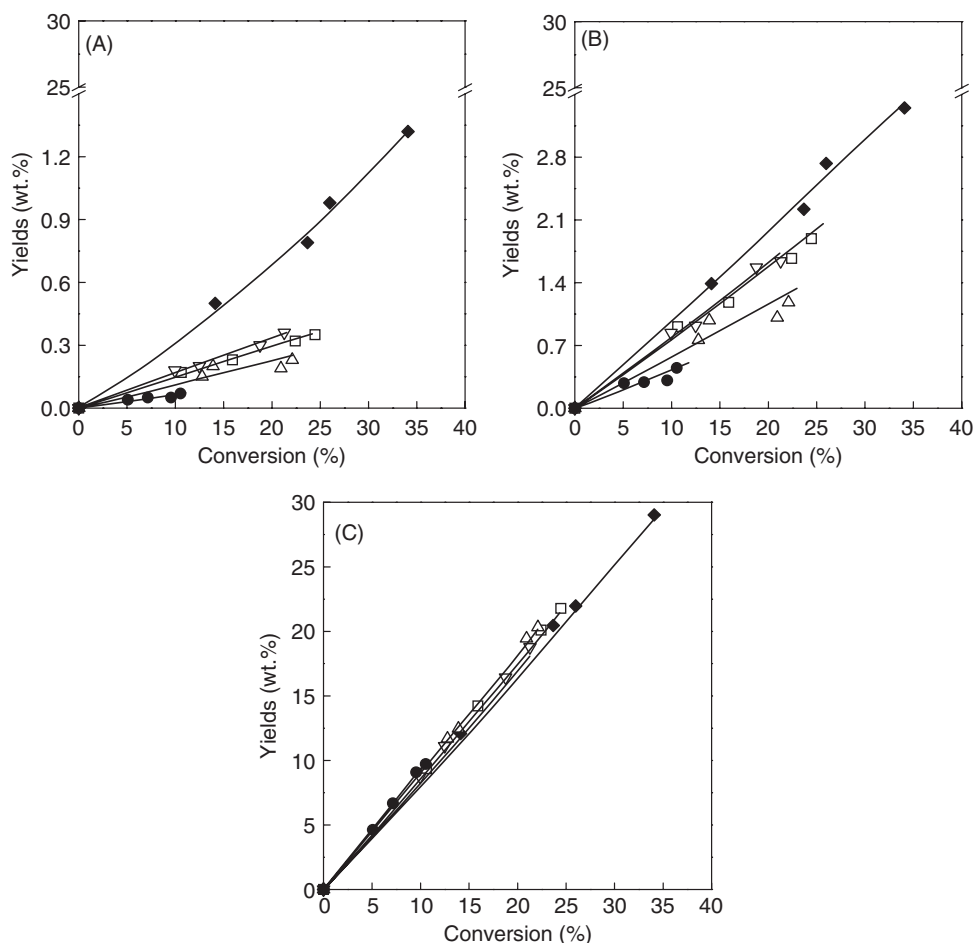


Figure 4. Yield curves of hydrocarbon groups from tetralin: (A) olefins, (B) paraffins–naphthenics, (C) aromatics. Symbols as in Fig. 1.

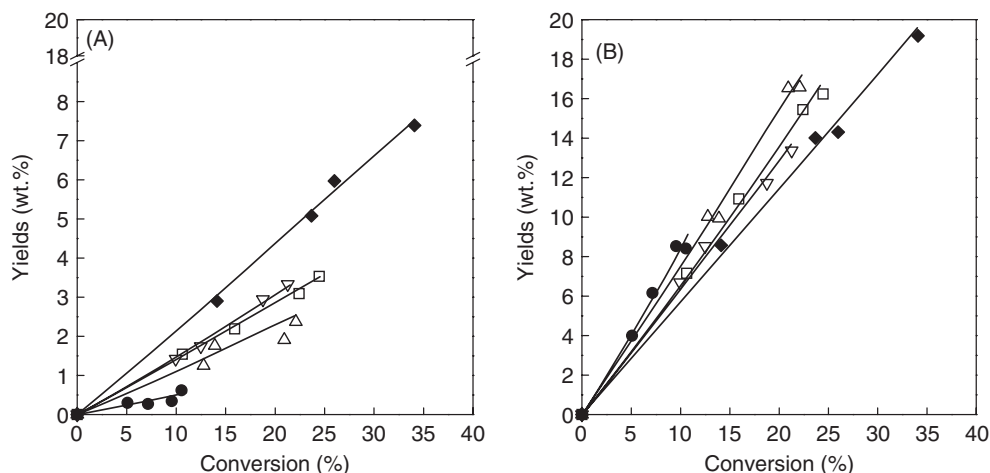


Figure 5. Yield curves of aromatic hydrocarbons from tetralin: (A) C_6 – C_9 , (B) C_{10} . Symbols as in Fig. 1.

When naphthalene was the reactant, essentially all the aromatics were light, benzene being the most important product; then, the yield curve is very similar to Fig. 3. However, intermediate aromatics, C_{10} , were not identified and heavy C_{11+} aromatics were observed only up to 0.25% yield. Olefins were produced at very low levels, under 0.2% with the fresh catalyst and 0.05% over the others, and paraffins were only observed with the most active catalysts, Cat-F, at 0.1% yield.

In reference to the formation of aromatics in the diesel range (C_{10} to C_{20} , or heavier), it was observed that their yields were significant only in the case of a naphthenic-aromatic reactant such as tetralin, including particularly C_{10} aromatics and low amounts of C_{11} – C_{14} aromatics, which included alkylated naphthenic-aromatics or di-aromatics, together with traces of phenanthrene and anthracene. From fully aromatics compounds such as naphthalene only very low yields of C_{11} – C_{12} aromatics were observed.

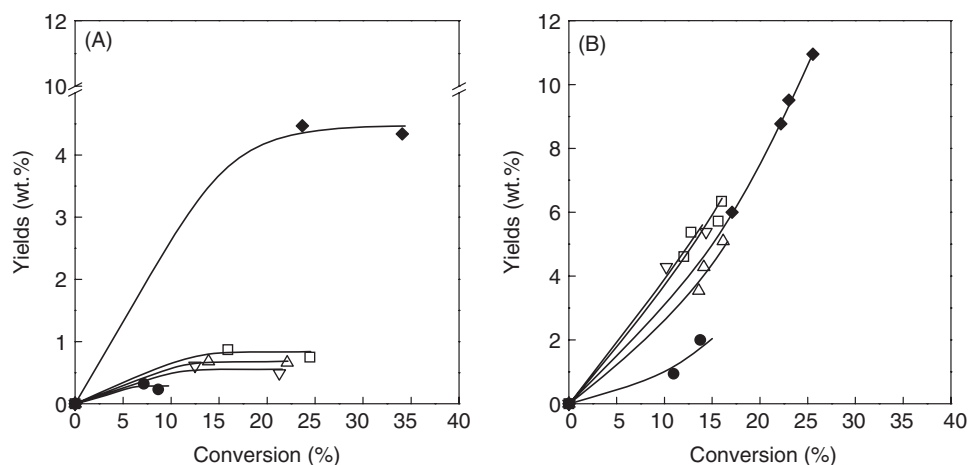


Figure 6. Coke yield curves: (A) tetralin, (B) naphthalene. Symbols as in Fig. 1.

Coke

The neat impact of the reactant type can be observed on coke yields in Fig. 6. In effect, the highest coke yields, showing a primary character, were observed with naphthalene, which has been used as a model reactant to study coke formation on ZrO/Al₂O₃/SiO₂ and silica–alumina catalysts.⁴⁷ On the contrary coke yields with tetralin were lower than 5%, including the most active catalyst (Cat-F). Moreover, the yield curves show flat profiles after certain reaction times (Fig. 6A). The more aromatic character and higher unsaturation of naphthalene in comparison to tetralin gives it a higher basicity and, consequently, a stronger trend to be adsorbed, protonated and condensed on the catalyst's acidic sites.⁴² On this basis, Appleby *et al.* concluded that coke yields in various acidic catalysts could be correlated with the basic character of aromatic compounds,⁴⁷ and Cerqueira *et al.* observed this specifically on HUSY zeolite.⁴⁸ Moreover, the naphthenic ring in tetralin molecules would be subjected to other reactions besides coking, thus decreasing its coke selectivity. Overall, aromatic compounds and, particularly, polyaromatic ones, are considered strong coke precursors, the order of reactivity to form coke being structure dependent, i.e. polynuclear aromatics > aromatics > olefins > branched alkanes > normal alkanes.⁴⁹

While the different coke-forming trend of each reactant is easily noticeable, the impact of the various catalyst properties is not, even though the extent and the rate of coke formation are also a function of the acidity and pore structure of the catalyst.⁴⁸ In effect, in the case of tetralin, the fresh catalyst produces much more coke than the others, a fact that could be related to the higher acidity of this catalyst. However, this difference is not observed in the case of naphthalene, where the yields of coke on Cat-F and the de-aluminated catalysts are very similar. Furthermore, it should be noted that coke formation on the equilibrated catalyst was the lowest with both reactants.

CONCLUSIONS

Based on the product distributions observed in the conversions of tetralin and naphthalene at 450 °C and short reaction times on FCC catalysts, a number of reactions can be proposed to define the corresponding reaction networks, with particular emphasis on aromatic products. In the case of tetralin, hydrogen transfer, ring opening and contraction and alkylation–disproportionation were

considered initial reactions. In the case of naphthalene, ring opening, hydrogen transfer and alkylation–disproportionation were considered initial reactions. Cracking reactions were considered as consecutive to ring opening.

The conversion of the naphthenic-aromatic reactant tetralin had hydrogen transfer as the most important reactions, their importance becoming more notable as long as the zeolite content and acidity in the catalysts became lower. Naphthalene, on the other hand, was particularly subjected to cracking reactions over all the catalysts.

According to the reaction paths proposed, aromatics are expected in the C₆–C₁₄ molecular range. Starting from tetralin, intermediate C₁₀ alkylated mono-aromatics and di-aromatics compounds are formed, among which naphthalene, the product from direct hydrogen transfer, is the most important product. Naphthalene produces more light C₉–alkylated mono-aromatic compounds.

The production of aromatics in the diesel range (C₁₀–C₂₀, or heavier), then, is important only in the case of tetralin. Since all the reaction paths from these test reactants lead to aromatic compounds, it is very difficult to avoid their occurrence in FCC.

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