

Catalytic Cracking of Heavy Aromatics and Polycyclic Aromatic Hydrocarbons over Fluidized Catalytic Cracking Catalysts

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ABSTRACT: The distribution of products in the range of gasoline and middle distillate cuts obtained in the catalytic cracking of heavy aromatics and polycyclic aromatic hydrocarbons over a fluidized catalytic cracking (FCC) catalyst was studied. 1-Phenyl octane, biphenyl, fluorene, 9,10-dihydrophenanthrene, naphthalene, phenanthrene, pyrene, and benz[*a*]anthracene were used as model compounds of alkylaromatic, naphthenic-aromatic, and polyaromatic hydrocarbons, which are present in vacuum gas oil and residual feedstocks in the FCC process. The catalyst was used in its fresh and equilibrium forms at 450 °C in a Chemical Reactor Engineering Centre Riser Simulator reactor with reaction times from 2 to 6 s. Thermal cracking reactions overwhelm the catalytic conversion of naphthenic-aromatic compounds, such as fluorene and 9,10-dihydrophenanthrene. Under the same conditions, the fresh catalyst was more active than the equilibrium catalyst. The alkylaromatic, naphthenic-aromatic, and polyaromatic hydrocarbons, showed catalytic conversions that increased, were relatively stable, and decreased, respectively, as a function of the reaction time. The distribution of products suggested that the most important reactions were thermal dehydrogenation, hydrogen transfer, ring opening, cracking, and condensation. It was shown that all of the model compounds are cracked, yielding particularly benzene in the gasoline range and coke.

1. INTRODUCTION

Currently, the growing demand to process larger volumes of lower quality crude oil or resids and the need to optimize the quality of light cycle oil “LCO” and maximize yields of petrochemical raw materials are some of the most complex issues in the oil-refining industry.^{1,2} As a consequence, changes are induced in the operation policies of the units of fluidized catalytic cracking (FCC) of hydrocarbons, which is one of the most important conversion processes in present refineries.

One of the drawbacks in the processing of residual or non-conventional hydrocarbon cuts, which are added to typical vacuum gas oil (VGO) feedstocks, is the conversion of extremely large molecular structures,³ particularly, fully aromatic structures, which are also present in VGOs. This may adversely affect the quality of fuels; for example, making the content of aromatic hydrocarbons in LCO very large (typically between 50 and 70%),⁴ a fact that induces a very low cetane index of about 24–28. In general, these issues are dependent upon the feedstock, the catalyst, and the process conditions.

However, the versatility of FCC in processing different low-quality, high-molecular-weight oil fractions opens new chances of improving fuel quality and yield by means of new catalysts producing less aromatics.^{5,6} The particles of FCC catalysts include Y zeolite as the main component supported on a matrix (active or inactive) together with various additives, fillers, and binders. At present, the catalysts are custom-made, according to the particular conditions in a refinery (feedstock, technology, and production scheme).^{6,7}

Then, if specific catalysts are to be developed to decrease the selectivity to aromatic hydrocarbons in middle distillate cuts, it is necessary to know the mechanisms controlling the formation of these compounds in the cut and the contribution to the

group from the various components in the feedstocks. The formation of aromatics in the heavy gasoline–LCO boiling range could be evaluated through the conversion of model compounds, which are present at significant concentrations in the feedstocks or among products.^{8,9} However, thus far, there exist few publications where the contribution from heavy polycyclic aromatic hydrocarbons (PAHs) in usual FCC feedstocks is investigated.^{10–12} On the contrary, more importance has been given to the study of the hydrogenation of polycyclic compounds,^{13–15} preferably naphthalene.^{16,17}

It is the objective of this work to study the conversion of alkylaromatic, naphthenic-aromatic, and polyaromatic hydrocarbons, which can be found in typical and residual cuts used as FCC feedstocks,^{18,19} with emphasis in the products belonging to the heavy end of gasoline and light end of LCO cuts, to generate useful information to assist in the formulation of new, more selective FCC catalysts. Eight different model reactants were used over the fresh and equilibrium forms of a commercial FCC catalyst in a Chemical Reactor Engineering Centre (CREC) Riser Simulator laboratory reactor under very short contact times.

2. EXPERIMENTAL SECTION

2.1. Materials. Both the fresh (Cat-F) and equilibrium (Cat-E) forms of a commercial FCC catalyst, which was formulated to maximize the LCO yield in the process, were used. The main catalyst properties are summarized in Table 1.

The total specific surface areas were calculated with the Brunauer–Emmett–Teller (BET) method, with $0.05 < P/P_0 < 0.3$, and the matrix

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Table 1. Properties of the Catalysts Used

catalyst	zeolite			RE content (wt %)	metals (Ni + V) content (wt %)	specific surface area (m ² g ⁻¹)		average mesopore diameter (nm)	acidity (μmol of Py g ⁻¹)					
									Brönsted (1545 cm ⁻¹)			Lewis (1450–1460 cm ⁻¹)		
	UCS (nm)	load (wt %)	Si/Al			matrix	total		150 °C	300 °C	400 °C	150 °C	300 °C	400 °C
	Cat-F	2.456	22.00			3.5	0.94		0.000	92	243	8.45	128.5	102.1
Cat-E	2.430	9.83	14.2	0.70	0.095	102	162	8.92	5.0	5.1	5.0	13.6	11.0	10.9

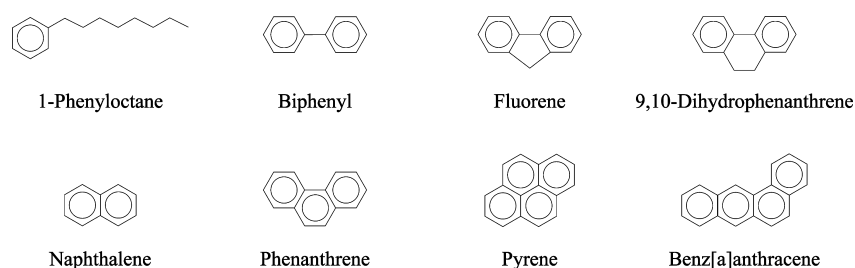


Figure 1. Schematic representation of the model reactants.

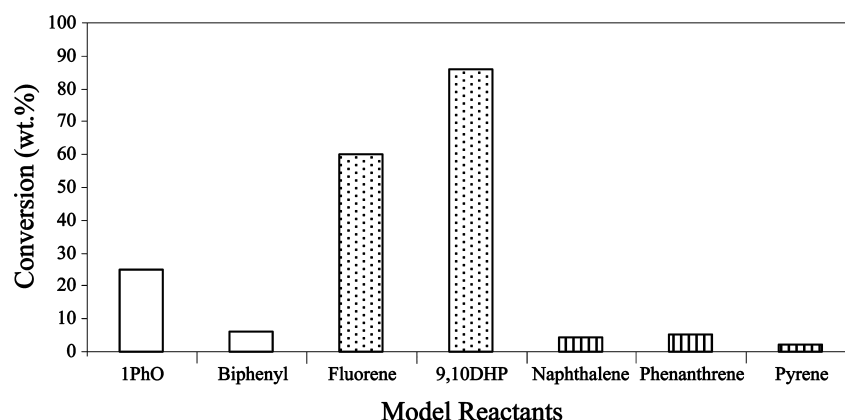


Figure 2. Thermal conversion of model reactants: (empty bars) alkylaromatics, (dotted bars) naphthenic aromatics, and (striped bars) condensed polyaromatics.

areas were calculated with the *t*-plot method, with $3.5 < t < 7.0$ Å, using N₂ adsorption isotherms at 77 K, obtained with Quantachrome Autosorb-1 equipment. The mesopore size distributions were calculated from the adsorption branch according to the Barrett–Joyner–Halenda (BJH) method,²⁰ and the zeolite content was determined from the micropore areas according to Johnson's method.²¹ The zeolite unit cell sizes (UCS) were determined with the ASTM D-3942-91 X-ray diffraction technique, using Shimadzu XD-1 equipment. The contents of rare earths were determined by means of the inductively coupled plasma (ICP) method, using a PerkinElmer optical emission spectrometer OPTIMA 2100 DV.

The nature, amount, and strength of acidic sites of both catalysts were determined by means of the Fourier transform infrared spectroscopy (FTIR) analysis of adsorbed pyridine (Merck, 99.5%) as a probe molecule in Shimadzu FTIR Prestige-21 equipment. 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 and 1450–1460 cm⁻¹, respectively, by means of the integrated molar extinction coefficients, which are considered independent from the catalyst and site strength.^{22,23}

The model reactants used were 1-phenyloctane (C₁₄H₂₂, 98%, Aldrich), biphenyl (C₁₂H₁₀, >99%, SAFC), fluorene (C₁₃H₁₀, 98%,

Aldrich), 9,10-dihydrophenanthrene (C₁₄H₁₂, 94%, Aldrich), naphthalene (C₁₀H₈, ≥99%, Merck), phenanthrene (C₁₄H₁₀, 97%, Fluka), pyrene (C₁₆H₁₀, >99%, Sigma), and benz[a]anthracene (BaA, C₁₈H₁₂, 99.5%, Supelco), with their schematic representation being shown in Figure 1. Because most of the reactants are solid at room temperature, they were dissolved in benzene (99%, Cicarelli) to feed them easily to the reactor. Concentrations were 10 wt % in all of the cases, except for naphthalene (25 wt %) and BaA (5 wt %). The conversion experiments were performed in a CREC Riser Simulator reactor, which is a batch, fluidized-bed laboratory reactor, which closely mimics the conditions of the commercial FCC process.²⁴ The unit has been described comprehensively elsewhere.^{25,26} Reaction times in the experiments were 2 and 6 s; reaction temperature was 450 °C, which is used in units operating in the middle distillate mode;²⁷ and mass catalyst/oil (solution) relationship was 1.12. The mass of catalyst was 0.15 g in all of the cases. Experiments of purely thermal cracking (no catalyst in the reactor) were performed at the same temperature under the longest reaction time.

2.2. Reaction and Analysis Equipment. The reaction products were analyzed by online standard capillary gas chromatography, using a 30 m long, 250 mm diameter, and 0.25 mm film thickness, nonpolar, dimethylpolysiloxane column. Product identification was performed with the help of standards and gas chromatography–mass spectrometry (GC–MS) analysis. The coke contents of the catalysts were assessed by means of a method with temperature-programmed

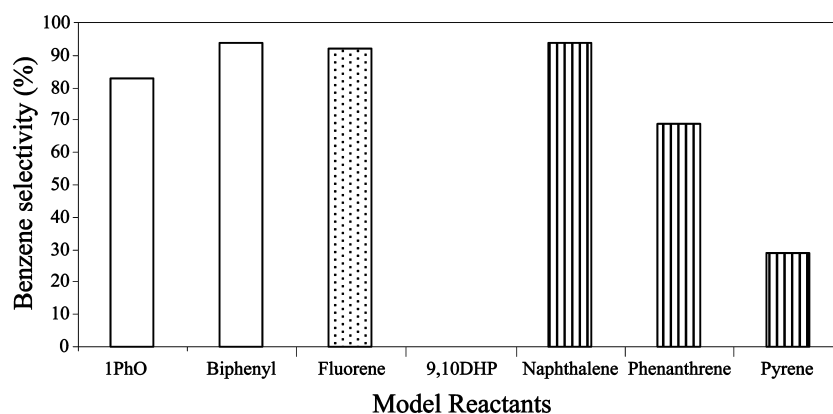


Figure 3. Selectivity to benzene in the thermal conversion of the model reactants: (empty bars) alkylaromatics, (dotted bars) naphthenic aromatics, and (striped bars) condensed polyaromatics.

oxidation and further methanation of the carbon oxides over a Ni catalyst and quantified with the help of a flame ionization detector (FID).²⁸ Mass balances (recoveries) closed to more than 95% in all of the cases.

3. RESULTS AND DISCUSSION

3.1. Reactivity of the Solvent. The experiments of thermal cracking of the pure solvent benzene showed conversions to be only 0.02%. This low conversion confirms the high thermal stability of benzene up to 1000 °C.²⁹

When pure benzene was fed to the catalytic beds of Cat-F and Cat-E, the maximum conversions observed were 0.35%, with coke being by far the most important product. These results show that benzene is essentially inert to form gaseous products under these reaction conditions, thus being a proper choice as a vehicle to feed the model reactants to the reactor, assuming that its conversion products would not interfere with the catalytic systems under study.

3.2. Thermal Cracking. Figure 2 shows the results of thermal cracking (no catalyst in the reactor) of the various model compounds at 6 s reaction time, where some trends can be appreciated according to their different chemical structures. These results can be rationalized in the light of the knowledge of the pyrolysis of hydrocarbons, which typically includes reversible reactions of free radicals,³⁰ the homolytic dissociation of covalent C–C or C–H bonds, and the β -scission reaction.³¹

The naphthenic-aromatic compounds (fluorene and 9,10-dihydrophenanthrene “9,10DHP”) are very reactive under thermal cracking reactions, with conversions that are as high as 86% in the case of 9,10DHP. The reactivity of alkylaromatic compounds (1-phenyloctane “1PhO” and biphenyl) is intermediate, with the highest conversion being 25% in the case of 1PhO. The condensed polyaromatic compounds whose molecules include fused benzene rings are the least reactive among the model compounds, with thermal cracking conversions lower than 5%. These results are consistent with observations from Al Darouich et al., who studied the thermal cracking of the (C₆–C₁₄) aromatic fraction of crude oil, including alkylaromatic and naphthenic-aromatic compounds, in the temperature range from 325 to 500 °C and reported that naphthenic-aromatic compounds were much less stable than alkylaromatic compounds.³²

Moreover, the difference in the thermal reactivities is particularly noticeable if similar structures, such as those of 9,10DHP (H/C = 0.86) and phenanthrene (H/C = 0.71), which differ in the central ring being saturated or unsaturated,

respectively, are compared. In effect, thermal conversions of 86% for 9,10DHP and 5% for phenanthrene were observed, thus confirming that the higher the unsaturation degree in a cyclic molecule, the higher its stability. This observation is also confirmed by the low thermal conversion shown by those molecules having fused aromatic rings (see Figure 2) and by the fact that, as the number of benzene rings in the molecule and its unsaturation degree increase, they become increasingly stable; for example, naphthalene converts to 4.55% and pyrene converts to 2.12%.

The higher reactivity provided by the naphthenic character in the molecular structures studied, as confirmed by the observations described previously (e.g., cases of reactants, such as fluorene and 9,10DHP; refer to Figure 2), was also noticed by Moldoveanu,²⁹ who suggested that cycloalkanes tend to form more stable compounds (highly unsaturated compounds) in the pyrolysis process. This behavior can be especially observed in the case of 9,10DHP (H/C = 0.86), which transforms into its analogous unsaturated phenanthrene (H/C = 0.71) by scission of the C–H bond in carbon atoms 9 and 10, with a selectivity of 99%. When fluorene, with a saturated ring of five C atoms, is the reactant, benzene was observed with selectivity of 92% (Figure 3), suggesting that the breaking of the C–C bond is favored.

In the case of alkylaromatics 1PhO and biphenyl, the latter is more stable, showing a thermal conversion of 5%. Perez and Raimondo also observed that a molecule that has some structural similarity to that of biphenyl, such as 1-phenyl-naphthalene, converted to only 1.5% when pyrolyzed at 450 °C.³³ On the other hand, the high selectivity to benzene observed with these model compounds can be justified on the basis of the dealkylation of the aliphatic side chain in 1PhO and the phenyl group in biphenyl (Figure 3), with this case leading obviously to a higher yield of benzene in producing two phenyl groups per reacted molecule. In the case of 1PhO, minor yields of toluene, ethylbenzene, xylenes, and C₂–C₈ olefins and paraffins besides benzene were also observed, which can be explained on the basis of the scission of the C₈ side chain. In that sense, Moldoveanu had reported that the formation of free radicals in the pyrolysis of alkylated aromatic hydrocarbons initiates with the scission of the bond between two carbon atoms with sp³ hybridation, particularly in the carbon atoms in the aliphatic side chain.²⁹ Moreover, Burklé-Vitzthum et al. mentioned that alkyl aromatics with long side chains show the weakest bond located at the β position in the side chain, close

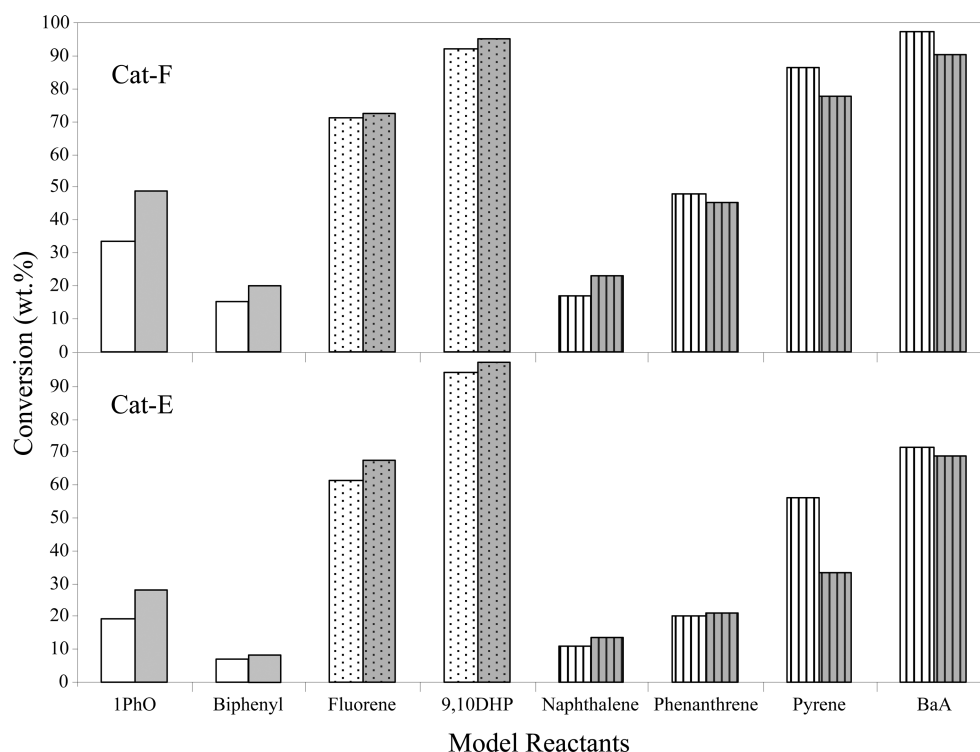


Figure 4. Conversion of the model reactants over catalysts Cat-F and Cat-E, with reaction times of (white bars) 2 s and (gray bars) 6 s: (empty bars) alkylaromatics, (dotted bars) naphthenic aromatics, and (striped bars) condensed polyaromatics.

to the ring; thus, cracking products, such as toluene and polyalkylbenzene, of short chains would be favored.³⁴

The condensed polyaromatic model compounds naphthalene, phenanthrene, and pyrene also showed important selectivities to benzene, although smaller than those of the other reactants, given their higher thermal stability and minor H/C (refer to Figure 3).

In summary, benzene is the main product in the thermal cracking of these model compounds, with the only exception of 9,10DHP, which shows phenanthrene as the most important product.

3.3. Catalytic Cracking. The conversions of the various model compounds over catalysts Cat-F and Cat-E are shown in Figure 4. In all of the cases, the conversions are higher on catalyst Cat-F than on catalyst Cat-E; this is expected, given the lower amount of crystalline material and acidic sites in the last catalyst, after being equilibrated in a commercial FCC unit. According to the values of thermal conversion shown in Figure 2, this process should be considered as part of the process of catalytic cracking and, for some of the model reactants, plays an important role, which is even more important at the low catalytic conversions observed on catalyst Cat-E.

Particularly, it can be considered that the overall catalytic cracking of naphthenic-aromatic compounds (fluorene and 9,10DHP) over both catalysts is essentially governed by the thermal cracking process. In the case of alkylaromatic compounds (1PhO and biphenyl), the contribution from the thermal reactions when they are converted on both catalysts Cat-F and Cat-E is expected to be considerable. A much lower contribution from thermal cracking to the overall conversion process is expected in the cases of the condensed polyaromatic compounds, particularly with molecules that include three or more unsaturated rings, where the catalytic effect can be noticed more significantly (Figures 2 and 4).

The reactivity observed in the case of 1PhO (linear C₈ alkyl aromatic) (Figure 4) confirms the observations by Corma et al. in the cracking of long side-chain alkyl aromatics over Y zeolite.³⁵ The eight carbon atom side chain is long enough to be subjected to the whole set of catalytic cracking reactions of hydrocarbons, as shown by the products, which are described later.

Moreover, if biphenyl, fluorene, and 9,10DHP, which are naphthenic-aromatic compounds, are considered similar structures with different numbers of carbon atoms (Figure 1), their conversions increased with the increasing number of carbon atoms in the molecules. The increasing conversions may be related to the naphthenic-aromatic structure, which makes the scission of the C–C and C–H bonds easier.³⁶ Appleby et al. also observed this behavior in studying the production of coke in catalytic cracking of naphthenic-aromatic and polyaromatic compounds over a fresh silica–alumina catalyst at 500 °C,¹¹ where the conversion of naphthenic-aromatic compounds was biphenyl (6.3%), fluorene (13.2%), and 9,10DHP (20.3%).

It was also observed in the case of the condensed polyaromatic hydrocarbons that conversion increased as long as the number of unsaturated ring increased (Figure 4), becoming close to those of the naphthenic-aromatic compounds, as a consequence of the production of coke. This is consistent with observations from Appleby et al., with naphthalene (7.7%), phenanthrene (16%), and pyrene (15.8%).¹¹ On the contrary, Dupain et al. in the cracking of an paraffinic gas oil spiked with model reactants, such as naphthalene, anthracene, and phenanthrene, observed an increase of their concentrations, particularly of naphthalene, thus concluding that cracking reactions in aromatic feedstocks are limited to alkylbenzenes or the paraffinic fraction.¹² These different behaviors observed if the condensed polyaromatic

Table 2. Selectivities of Benzene and Coke (%) in the Catalytic Cracking of the Model Compounds

reaction time (s)	Cat-F				Cat-E			
	benzene		coke		benzene		coke	
	2	6	2	6	2	6	2	6
1PhO	51.94	36.46	21.59	26.33	74.64	63.29	9.59	14.04
biphenyl	64.93	55.75	32.56	42.21	82.02	67.43	14.66	28.59
fluorene	78.75	79.52	7.24	11.53	89.48	87.27	2.50	4.61
9,10DHP	12.27	14.38	9.45	15.10	14.77	11.69	2.00	4.08
naphthalene	60.68	51.02	35.11	41.29	87.86	83.43	8.58	14.53
phenanthrene	66.37	49.75	25.14	44.65	76.11	60.10	15.91	32.01
pyrene	96.74	93.50	2.62	5.66	92.55	75.32	5.73	20.93
BaA	80.04	67.76	16.87	29.18	89.35	80.49	8.05	17.51

hydrocarbons are fed pure (this work and Appleby et al.¹¹) or taking part of a complex mixture, such as gas oil (Dupain et al.¹²), can be explained if it is considered that they do not compete for acidic sites with other hydrocarbons. Pujro et al. found that the isolated fractions (saturated, aromatic, and resin) of atmospheric tower resid (ATR) convert extensively when reacted under FCC conditions over commercial equilibrium catalysts at 550 °C.³⁷ However, the differences in the yields of the main hydrocarbon groups from the various fractions are noteworthy and reveal their nature; moreover, it is not possible to assess the yields of given groups from the conversion of the resid by the direct addition of the yields from the different fractions, because of interactions among the various fractions and the corresponding products.

It can be seen in Figure 4 that longer reaction times impact differently on the various model reactants. In effect, the increase in conversion as a function of the reaction time was very important in the case of 1PhO (about 15% over Cat-F and 7% over Cat-E) and moderate in the cases of biphenyl, fluorene, and 9,10DHP (less than 5% for both catalysts). In the case of condensed polyaromatic hydrocarbons, naphthalene showed a moderate increase, while phenanthrene, pyrene, and BaA showed a decrease in their conversions after increasing the reaction time, which was very significant in the case of pyrene and BaA. This different behavior for condensed polyaromatic compounds, as compared to alkylaromatic and naphthenic-aromatic compounds, can be assigned to their higher yield of coke, which induces catalyst deactivation. Condensed polyaromatic compounds are considered strong coke precursors, or they may strongly adsorb on acidic catalysts. It was reported in studies about coke oxidation on Y zeolite with pyrene as the model compound³⁸ that the amount of pyrene adsorbed corresponded to approximately 1 molecule per supercage, with TPO experiments showing that more than 90% of the adsorbed pyrene molecules was recovered as CO and CO₂, demonstrating that this type of molecule can be strongly adsorbed on the zeolite surface.

3.4. Reaction Products. The occurrence of unsaturated rings in the molecules of the model compounds suggests that the set of reactions would initiate through the electrophilic attack of acidic protons in the catalyst surface. This was also proposed in the cracking of alkylated benzenes, such as isobutyl benzene,³⁹ of molecules, such as tetralin and naphthalene,⁴⁰ and in the formation of coke from benzene,⁴¹ because the benzene rings are a rich source of electrons (nucleophile)³⁶ and the resonating character favors the formation of a positive, also resonating, species, which is known as a benzylic carbocation, with a stability similar to that of a secondary carbocation.⁴²

A heterogeneous group of products with 1–14 carbon atoms per molecule, including C₁–C₂ light gases, C₃–C₆ olefins, C₄–C₈ paraffins, C₆–C₈ naphthenics, benzene, toluene, xylenes, indane, dimethylindane, and smaller amounts of decalin, tetralin, naphthalene, biphenyl, methyl naphthalene, and phenanthrene, is the consequence of the conversion of 1PhO (Bz-C₈). A set of reactions is to be expected; for example, dealkylation reactions, which can be complemented by the cracking, disproportionation, and cyclization reactions of C₈ olefinic chains.⁴³ In effect, the side chain can be protonated and suffer scission at different locations and even cyclization to produce tetralin, followed by hydrogen-transfer reactions that lead to naphthalene. These reactions and their corresponding products are consistent with the observations by Watson et al. about the reaction pathways in the catalytic cracking of alkylbenzenes (including phenyloctane) over rare earth Y (REY) at 500 °C.⁴⁴ These authors propose that the reactions initiate via protonation of the aromatic ring or paraffin adsorption of the alkyl side chain, forming a five-centered carbonium ion and giving place to dealkylation by β -scission. Moreover, Corma et al. identified three main routes in the cracking of alkylaromatics with long side chains over USY zeolite at 500 °C: dealkylation of the benzene ring to yield benzene and an olefin, protolytic cleavage of the alkyl side chain to yield an olefin and an alkyl benzene or a paraffin and an alkenyl benzene, and alkylation of an intermediate alkylaromatic with short-chain olefins, followed by ring closing.^{35,45}

Minor productions (<0.5 wt %) of light gases, toluene, xylenes, and naphthalene were observed in the cracking reaction of biphenyl, together with the most important products benzene and coke (Table 2), thus suggesting that the dealkylation of phenyl groups, promoted by the formation of a benzylic carbocation,³⁹ is the most important reaction. Coke could be the consequence of oligomerization and condensation reactions.

Among the products from the catalytic cracking of fluorene, a naphthenic-aromatic compound, low yields (<0.5 wt %) of light gases, C₇–C₁₀ alkylbenzenes, tetralin, indane, biphenyl, and naphthalene were observed, together with significant yields of a phenanthrene isomer (C₁₄H₁₀), benzene, and coke, suggesting that it undergoes the ring-opening reaction in its five-member saturated ring and further cracking of the biphenyl-type bridge (Ph–Ph), following a reaction scheme similar to that of biphenyl. In the catalytic cracking of fluorene over silica–alumina at 500 °C, Appleby et al. observed a yield of 1.3 wt % H₂,¹¹ suggesting that the molecule dehydrogenates through either the thermal hemolytic scission of the C–H bond on carbon number 9 or the hydrogen-transfer reaction on the acidic sites of the catalyst.

However, in the case of 9,10DHP, the experimental conditions in this work promote its thermal cracking reactions, making phenanthrene the most important product in its catalytic conversion, given the dehydrogenation of the saturated ring. Even so, minor yields (<1 wt %) of light gases, benzene, toluene, ethylbenzene, biphenyl, and C_2 – C_5 olefins and paraffins were observed, suggesting that the saturated ring can be opened and the biphenyl-type bridge can be further cracked on the catalyst acidic sites. Experiments of hydroconversion of phenanthrene over bifunctional metal/acid catalysts showed hydroaromatic compounds among the products, including 9,10DHP,¹³ suggesting that it could suffer the opening of its saturated six-member ring following a purely acidic mechanism, to be initiated with the formation of either a benzylic or secondary carbocation by the attack of the surface protons to the external aromatic rings.

In condensed polyaromatic molecules, the action of the zeolite protons would favor the stability of the unsaturated rings located at the extreme positions, as shown in reactions of electrophilic substitution of polyaromatic compounds,³⁶ a fact also observed in the catalytic cracking of naphthalene on FCC catalysts.⁴⁰ In relation to this, Korre and Klein studied the hydrogenation of heavy oil, evaluating the impact of the structure of fully aromatic compounds with one to four aromatic rings, and confirmed that central aromatic rings are preferentially saturated against extreme rings.¹⁴ Intermediate compounds with partially saturated rings are susceptible to ring opening and further cracking of the biphenyl-type bridge (Ph–Ph), similar to 9,10DHP, thus explaining the occurrence of light gases, benzene, toluene, xylenes, naphthalene, and coke from phenanthrene, pyrene, and BaA. Particular products can be identified from the conversion of each model compound, for example, fluorene and phenanthrene from pyrene and biphenyl, phenanthrene, and pyrene from BaA.

Hydrogen needed for the saturation of whichever aromatic ring in the hydrogen-transfer reactions could be provided by the dehydrogenation reaction in the thermal cracking steps or the formation of coke from the own model reactants. For example, Appleby et al. reported a yield of gases of 1.2 wt % (76% hydrogen) in the catalytic cracking of phenanthrene and a yield of gases of 1.9 wt % (84% hydrogen) in the catalytic cracking of pyrene.¹¹

In summary, it was shown that all of the model reactants can be cracked by this acidic catalysts, demonstrating that both thermal (homolytic C–C and C–H scissions) and catalytic (hydrogen transfer, cracking, dealkylation, cyclization, and oligomerization) reactions occur simultaneously, giving place to high benzene and coke yields (Table 2) and much lower yields of light gases and liquids (<1 wt %). Conversions increased with the number of carbon atoms per molecule, and as expected, they were higher on the fresh catalyst (Figure 4).

If the thermal and catalytic selectivities of benzene in the experiments with alkylaromatic reactants 1PhO and biphenyl are compared (Figure 3 and Table 2), it can be seen that they were lower in the experiments with both catalysts. This fact can be explained in light of the catalysts promoting reactions other than dealkylation (which was the only one in the thermal experiments); also, the formation of coke on the catalysts has to be considered (Table 2), which could certainly consume part of the benzene molecules.

In the case of the naphthenic-aromatic compounds, it was observed that, for the case of fluorene, the selectivity to benzene does not change when the catalyst is present, even

though other reactions and coke formation occur, where benzene can take part. On the contrary, the catalysts favor the production of benzene from 9,10DHP, thus confirming that the catalysts promote the ring-opening reactions.

The selectivity to benzene in the catalytic conversion of condensed polyaromatic molecules shows that it is possible to crack these highly condensed hydrocarbon molecules on these acidic catalysts at FCC conditions.

In general, longer reaction times produced a decrease in benzene yields, together with an increase in coke yields (see Table 2), strongly suggesting that benzene is involved in the production of coke. In the cases of phenanthrene, pyrene, and BaA, the yield of coke could not be considered exclusively on the basis of the consumption of benzene and other reaction products but also on the own reactants, given their strongly aromatic character, which makes them coke precursors. This fact is reflected on the decrease in the conversions of these model reactants as a function of time (see Figure 4). Moreover, it can be seen in Table 2 and Figure 4 that the yields of coke increase as the number of carbon atoms per molecule increases, as also observed by Appleby et al.¹¹ and Corma et al.⁴⁶

4. CONCLUSION

Various model compounds (alkylaromatic, naphthenic-aromatic, and condensed polyaromatic hydrocarbons), which are usually present in residual or VGO feedstocks to the FCC process, showed differences in both their thermal and catalytic conversions on FCC catalysts. The thermal cracking of naphthenic-aromatic compounds at 450 °C was the highest among the model compounds used, less important for alkylaromatics, and very low for the condensed polyaromatics. Particularly for fluorene and 9,10DHP (naphthenic-aromatic compounds), the thermal cracking reactions govern the total conversion process.

The catalytic conversions were the highest over the fresh catalyst Cat-F, which has a higher content of zeolite and acidity. The distributions of products showed that most important reactions were the thermal cracking when no catalyst was present and hydrogen transfer, ring opening, cracking, and condensation when catalysts were used, which are initiated by the electrophilic attack of protons on the surface of the Y zeolite.

It was shown that all of the model compounds are cracked, yielding particularly benzene in the gasoline range and coke.

These conclusions could support the formulation of FCC catalysts aimed at selectively cracking given types of hydrocarbons, according to the compositions of the feedstocks.

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■ REFERENCES

- (1) Philips, G. *Pet. Technol. Q.* **2002**, 93–99.
- (2) European Union. *Off. J. Eur. Union* **2009**, 52 (L140), 88–113.
- (3) Yung, K. Y.; O'Connor, P. O.; Janik, S. J.; Bruno, K. *Catal. Cour.* **2003**, 53, 2–8.
- (4) UOP. *Diesel Fuel. Specifications and Demands for the 21st Century*; UOP LLC: Des Plaines, IL, 1998; pp 17–28.
- (5) Corma, A.; Martínez, C.; Sauvanaud, L. *Catal. Today* **2007**, 127, 3–16.
- (6) Gilbert, W. R.; Morgado, E., Jr.; de Abreu, M. A. S.; de la Puente, G.; Passamonti, F.; Sedran, U. *Fuel Process. Technol.* **2011**, 92, 2235–2240.
- (7) Hoffman, H. L. *Hydrocarbon Process.* **1990**, 69, 53–54.
- (8) Corma, A.; Mocholi, F.; Orchilles, V.; Koermer, G. S.; Madon, R. *J. Appl. Catal.* **1991**, 67, 307–324.
- (9) de la Puente, G.; Sedran, U. *Appl. Catal., A* **1996**, 144, 147–158.
- (10) Greensfelder, B. S.; Voge, H. H.; Good, G. M. *Ind. Eng. Chem.* **1945**, 37, 1168–1176.
- (11) Appleby, W. G.; Gibson, J. W.; Good, G. M. *Ind. Eng. Chem. Process Des. Dev.* **1962**, 1, 102–110.
- (12) Dupain, X.; Gamas, E. D.; Madon, R.; Kelkar, C. P.; Makkee, M.; Moulijn, J. A. *Fuel* **2003**, 82, 1559–1569.
- (13) Lemberston, J. L.; Guisnet, M. *Appl. Catal.* **1984**, 13, 181–192.
- (14) Korre, S. C.; Klein, M. T. *Ind. Eng. Chem. Res.* **1995**, 34, 101–117.
- (15) Chareonpanich, M.; Zhang, Z.-G.; Tomita, A. *Energy Fuels* **1996**, 10, 927–931.
- (16) Liu, X.; Smith, K. J. *Appl. Catal., A* **2008**, 335, 230–240.
- (17) Ardakani, S. J.; Smith, K. J. *Appl. Catal., A* **2011**, 403, 36–47.
- (18) Satou, M.; Itoh, D.; Hattori, H.; Yashida, T. *Fuel* **2000**, 79, 339–348.
- (19) Parastar, H.; Radovic, J. R.; Jalali-Heravi, M.; Diez, S.; Bayona, J. M.; Tauler, R. *Anal. Chem.* **2011**, 83, 9289–9297.
- (20) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, 73, 373–380.
- (21) Johnson, M. F. L. *J. Catal.* **1978**, 52, 425–431.
- (22) Emeis, C. A. *J. Catal.* **1993**, 141, 347–354.
- (23) Renzini, M. S.; Sedran, U.; Pierella, L. B. *J. Anal. Appl. Pyrolysis* **2009**, 86, 215–220.
- (24) de Lasa, H. I. U.S. Patent 5,102,628, 1992.
- (25) Passamonti, F.; de la Puente, G.; Morgado, E.; Gilbert, W.; Sedran, U. *Chem. Eng. J.* **2012**, 183, 433–447.
- (26) Al-Khattaf, S. *Ind. Eng. Chem. Res.* **2007**, 46, 59–69.
- (27) *Chemical Reactor Technology for Environmentally Safe Reactors and Products*; de Lasa, H. I., Dogu, G., Ravella, A., Eds.; Springer: Dordrecht, Netherlands, 1993; Vol. 225, Nato Science Series E, pp 17–50.
- (28) Fung, S. C.; Querini, C. A. *J. Catal.* **1992**, 138, 240–254.
- (29) Moldoveanu, S. C. *Techniques and Instrumentation in Analytical Chemistry*; Elsevier: Amsterdam, Netherlands, 2010; Chapter 7, pp 131–229.
- (30) Savage, P. E. *J. Anal. Appl. Pyrolysis* **2000**, 54, 109–126.
- (31) Poutsma, M. L. *J. Anal. Appl. Pyrolysis* **2000**, 54, 5–35.
- (32) Al Darouich, T.; Behar, F.; Largeau, C. *Org. Geochem.* **2006**, 37, 1130–1154.
- (33) Perez, G.; Raimondo, M. *Chemosphere* **1996**, 32, 1301–1305.
- (34) Burklé-Vitzthum, V.; Michels, R.; Scacchi, G.; Marquaire, P. M.; Dessort, D.; Pradier, B.; Brevart, O. *Org. Geochem.* **2004**, 35, 3–31.
- (35) Corma, A.; Miguel, P. J.; Orchillés, A. V.; Koermer, G. S. *J. Catal.* **1992**, 135, 45–59.
- (36) Morrison, R. T.; Boyd, R. N. *Química Orgánica*, 2nd ed.; Fondo Educativo Interamericano S.A. de C.V., Mexico City, Mexico, 1985; pp 574–624.
- (37) Pujro, R.; Falco, M.; Devard, A.; Sedran, U. *Fuel* **2014**, 119, 219–225.
- (38) Moljord, K.; Magnoux, P.; Guisnet, M. *Catal. Lett.* **1994**, 28, 53–59.
- (39) Lemberston, J. L.; Baudon, A.; Guisnet, M.; Marchal, N.; Mignard, S. *Stud. Surf. Sci. Catal.* **1997**, 106, 129–136.
- (40) Pujro, R.; Falco, M.; Sedran, U.; *J. Chem. Technol. Biotechnol.* DOI: 10.1002/jctb.4570.
- (41) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; pp 1–111.
- (42) McMurry, J. *Química Orgánica*, 7th ed.; Cengage Learning Editores S.A. de C.V.: Mexico City, Mexico, 2008; pp 516–146.
- (43) Smirniotis, P. G.; Ruckenstein, E. *Ind. Eng. Chem. Res.* **1994**, 33, 800–813.
- (44) Watson, B. A.; Klein, M. T.; Harding, R. H. *Appl. Catal., A* **1997**, 160, 13–39.
- (45) Corma, A.; Miguel, P. J.; Orchillés, A. V.; Koermer, G. *J. Catal.* **1994**, 145, 181–186.
- (46) Corma, A.; Miguel, P.; Orchillés, A. *J. Catal.* **1994**, 145, 171–180.