

FCC Catalyst Accessibility—A Review

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Abstract: Fluid catalytic cracking (FCC) is a critical process in the petroleum-refining industry, designed to break down large hydrocarbon molecules into smaller, more valuable products. Fluid-cracking catalyst accessibility dramatically influences the efficiency of the FCC process. Accessibility is a catalyst feature related to the ease with which large feedstock molecules can penetrate the catalyst particle to reach the internal active sites where reactions occur—and the ease with which products desorb and leave the catalyst. Accessibility plays a vital role in the activity, selectivity, and life of the catalyst, and various techniques can be applied during the manufacturing process to accomplish its increase. This work reviews FCC catalyst accessibility, its characterization, and the ways to increase it, covering the past three decades of technical paper and patent literature. Bibliometric results of a literature search are presented, and a search strategy is described, encompassing database identification, keyword selection, refinement terms, search criteria, and result evaluation.

Keywords: FCC; catalyst; accessibility; mesochemistry; connectivity



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1. Introduction

The fluid catalytic cracking (FCC) process has been the most profitable and flexible refining process for almost 80 years, both because it is the chief heavy fraction-upgrading process and due to its ability to meet changing demands [1]. Its main goal is to convert high-boiling oil fractions called gas oil into high-value, high-octane gasoline, diesel, kerosene, LPG, and heating oil [2]. Gas oil is the portion of crude oil that commonly boils in the 330-to-550 °C range. Depending on the type of oil, process feed can range from vacuum gas oil (VGO) to atmospheric residue (ATR), not to mention unconventional feeds such as tight oil or heavy feeds (tar sands and bitumen).

In an FCC converter, the catalyst is mixed with feedstock at the bottom of the riser reactor. Cracking reactions cause the reactant mixture to expand as gases form, and the catalyst–feedstock mixture flows upwards to enter the riser reactor at ca. 40 m/s. Therefore, the typical contact time in a riser is in the order of seconds [3].

Because of the reduced reaction time, reaction severity should be high to maintain suitable conversion. The diffusion of the heavy, large reactant molecules through the catalyst pores to the reaction sites is essential to determine the overall reaction rate. In addition, reaction products must quickly diffuse out of the catalyst particle to prevent overcracking to light products and other undesirable secondary reactions such as coke formation. The term accessibility has been used to describe these phenomena [4].

The first commercial fluid catalytic cracking plant (Model I, upflow design) started up at Standard Oil of New Jersey's (ESSO) Baton Rouge refinery (Louisiana), processing 2100 m³/d (13,000 bpd, barrels per day) of oil on 25 May 1942 [2]. Cracking catalyst systems have been evolving continuously for over 80 years, and catalysts are still at the heart of the FCC process. Worldwide FCC catalyst production in 2013 was ca. 600 kta (kilotons per annum) with a market value of over USD 1.6 billion and an Average Annual Growth Rate (AAGR) of 3% [5].

1.1. FCC Process Description

The cracking process takes place in the converter of an FCC Unit, FCCU (Figure 1 [3]). Preheated feed enters the bottom of the riser through the injection nozzle, where it is dispersed with the atomizing steam and readily vaporizes and expands as it encounters the hot regenerated catalyst. Cracking reactions begin as the feed vaporizes and continue within 1.5 to 3.0 s as the vapors travel up along the riser.

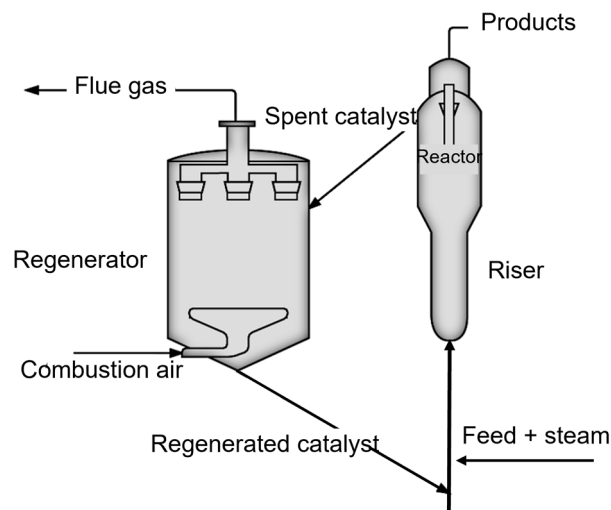


Figure 1. Schematic depiction of a Fluid Catalytic Cracking Unit (FCCU).

The catalyst-to-oil ratio (CTO) is usually in the range of 4:1 to 9:1 by weight (catalyst kg:t feed). The heat absorbed by the catalyst in the regenerator provides the energy to:

- heat the feed from the injection temperature to the desired reaction temperature (TR_x).
- supply heat for the endothermic cracking reactions occurring in the riser.
- heat the air blown to the regenerator, from the discharge temperature to the flue gas outlet temperature.
- make up for heat losses in the unit.

The riser is a vertical pipe that ideally simulates a plug flow reactor, along which the catalyst and vaporized feed travel with minimum back mixing. Efficient contacting of the feed and catalyst is critical to achieving the desired reactions. The operating pressure is low, and the reaction temperature ranges from 500 °C to 540 °C.

Catalyst and the products separate quickly in the cyclones inside the reactor. The collected catalyst returns to the stripper through the diplegs. Product vapors exit the cyclones and flow to the main fractionator for recovery [2].

The spent catalyst enters the stripper carrying hydrocarbon vapors that are adsorbed on its surface and fill its pores. Stripping steam is used primarily to remove the hydrocarbons entrained among individual catalyst particles, but it does not remove those that have filled the catalyst's pores.

Coke can deposit on the spent catalyst in amounts of 0.4–2.5 wt.%, depending on the feedstock quality and regenerator combustion regime (partial or total). The catalyst flows to the regenerator to burn off coke and restore its activity. The regenerator temperature typically ranges from 680 to 720 °C but can reach 760 °C, depending on oxygen availability. In short, the regenerator has two main functions: it restores catalyst activity and supplies heat to crack the feed [3].

One or more air blowers provide sufficient air velocity and pressure to maintain the catalyst bed in a fluid state. Air enters the regenerator through a distributor near the vessel's bottom to supply oxygen to burn the coke.

1.2. The Catalyst

The FCCU uses a microspherical fine powder as a catalyst, with an average particle size (APS) of ca. 75 μm , which behaves like a fluid when properly aerated (fluidized) in the converter.

FCC catalyst is of paramount importance for the performance of the unit. The nature of the feed, FCCU objectives, and constraints are the primary drivers for catalyst formulation.

The literature on fluid-cracking catalyst manufacturing describes two general techniques to embed the active zeolitic and structural components into the microspheres: the additive and the in situ. The zeolite is crystallized separately in the additive technique and then incorporated into microspheres with the other ingredients and a suitable binder. The in situ technique uses a spray-dryer to first form the microspheres, upon which the zeolite crystallizes to provide particles containing both zeolitic and non-zeolitic components [6].

The binding system must keep the catalyst's physical integrity in the FCC converter while maintaining the catalytic activity. The challenge of choosing the binder lies in its efficiency in minimizing material loss due to particle breakage without compromising catalyst accessibility, i.e., the diffusion control of feed molecules and products obtained by cracking.

The study of binder-ingredient interaction involves fundamental knowledge of surface phenomena, heterogeneous catalysis, and compounding technology (particle composition and formatting).

1.2.1. FCC Catalyst Compounding

A typical FCC catalyst is a composite of catalytically active and non-active ingredients that impart physical properties to it, as depicted in Figure 2 (adapted from Vogt and Weckhuysen [3]):

1. An active component (Zeolite): modified Y zeolite (faujasite, FAU) containing rare earth (RE) elements, mostly lanthanum (La) and cerium (Ce), and small amounts of neodymium (Nd) and praseodymium (Pr)—or no rare earth at all—is responsible for the catalyst activity and selectivity towards naphtha make. Other zeolites can be added to the catalyst formulation, such as MFI type, to increase LPG make, propylene yield, and octane number. As-synthesized Y zeolite contains sodium ions that must be removed to render it active for the cracking reactions and increase its stability towards acid and hydrothermal treatments [7]. La^{3+} and Ce^{3+} are introduced by ion exchange for Na^{+} (rare earth Y zeolite, REY), but one cannot obtain the acidic form of zeolite Y (HY) by direct exchange with acids, which could destroy the zeolite framework. Protons (H^{+}) are thus indirectly introduced by NH_4^{+} exchange followed by calcination to remove NH_3 . Protons may also be introduced in REY via a hydrolysis reaction catalyzed by RE-cations [8,9].
2. An active matrix: mesoporous alumina with the ability to improve bottom cracking, i.e., cracking of large, high-boiling-point molecules. After undergoing cracking, said molecules turn smaller, suited to enter the zeolite micropores. Large crystal aluminas can also passivate (trap) Ni. The active matrix should have large pores to minimize pore collapse and sintering and to allow for the rapid transport of large molecules (slow mass transport will lead to overcracking and coking) [2]. Large pores and low specific area decrease the dispersion of contaminant metals, therefore increasing the catalyst metal resistance. On the other hand, small pores increase the carryover of heavy molecules present as liquids into the regenerator, where they will burn, a product loss that impacts FCCU profitability.
3. An inert matrix: clay (usually kaolin) embedded as a filler in the catalyst to impart structural integrity to it and dilute its activity. The inert matrix itself has no catalytic activity.
4. A synthetic matrix (Binder): polymerized silica, alumina, aluminosilicate, or aluminum phosphate can serve as a glue to hold the zeolite, matrix, and clay together. The binder may or may not have catalytic activity. Clay and binder should provide

physical integrity (density, attrition resistance, particle size distribution), heat transfer medium, and fluidization medium in which the more valuable zeolite component is incorporated [3].

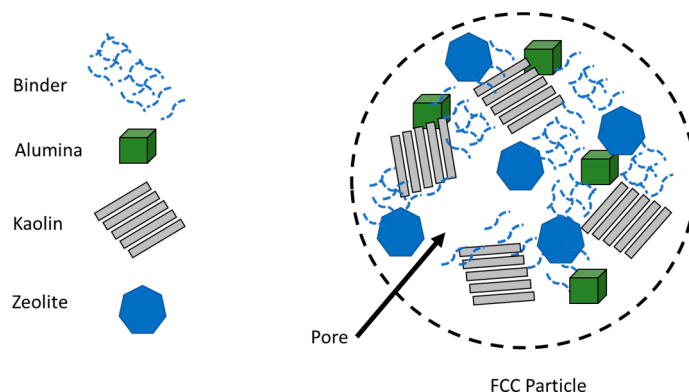


Figure 2. Typical chemical and structural composition of an FCC particle.

The components' nature and processing history and catalyst drying conditions determine the physicochemical properties of FCC particles.

1.2.2. Chemical Composition

The catalyst composition can be determined by X-rays Fluorescence (XRF) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS), the results of which agree satisfactorily [10].

1. Sodium (wt.%): the syntheses of the catalyst's main ingredients occur in a Na-rich environment. The catalytic activity of acidic zeolites strongly depends on the degree of Na removal. For maximum Brønsted acid activity, deep removal of sodium or other bases is essential [11]. Sodium Levels below 0.5 wt.% are the typical figures in this industry.
2. Rare Earth (wt.%): Rare Earth (RE) content comes from the amount of zeolite in the catalyst (provided there is no other source intentionally added to the formulation). The higher the RE level, the more active and selective towards gasoline the catalyst. However, high RE-content catalysts will produce low-octane-rate gasoline.

1.2.3. Particle Size Distribution (PSD)

Particle size and density are essential for attrition resistance and fluidizability. The optimum particle size distribution (PSD) for fluidization is specific for each FCC unit. Small particles are undesirable because of fines loss [12].

PSD is routinely measured in laboratories for production quality control and FCC unit monitoring. ASTM D4464-15(2020) Standard Test Method for Particle Size Distribution of Catalytic Materials by Laser Light Scattering describes the standard procedures to determine FCC PSD, applied with minor adaptations from site to site. PSD can also be determined by a set of wire mesh sieves with openings from 20 to 149 μm .

FCCU project design enables it to handle particles with sizes in the range of 40 to 105 μm , the average particle size (APS) being 75 μm . Larger sizes may break or not circulate smoothly, and the unit will cut (lose) all particles below 40 μm .

1.2.4. Textural Properties

Heterogeneous catalysis is a surface phenomenon, the extension of which is a function of the area available to the reacting molecules. Area and porosity are determined by nitrogen adsorption methods described in standard procedures:

- ASTM D4222-20 Standard Test Method for Determination of Nitrogen Adsorption and Desorption Isotherms of Catalysts and Catalyst Carriers by Static Volumetric Measurements: Specific Area, SA—total area per unit mass of the catalyst (m^2/g)
- ASTM D4365-19 Standard Test Method for Determining Micropore Volume and Zeolite Area of a Catalyst: Micropore Volume (MiPV), which is the total volume of micropores per unit mass (cm^3/g), associated with the available zeolite content in the catalyst, and meso Specific Area (mSA), i.e., external and mesopores area per unit mass (m^2/g) of the material.

1.2.5. Accessibility

Accessibility is a catalyst feature related to the ease with which large molecules can penetrate it to reach the internal acid sites where reactions occur. Although textural properties are static, averaged figures, accessibility is a dynamic measurement that can be assessed by different penetration techniques [13].

AAI measurement is based on the liquid-phase diffusion of large organic molecules into the catalyst. A probe molecule and a solvent circulate through a stirred vessel and an inline spectrophotometer. The probe molecule is chosen to simulate high molecular weight hydrocarbons with a boiling point well above 480°C . Such large molecules cannot enter the zeolite channels, and their effective diffusivity strongly depends on the catalyst's pore system. The test determines the catalysts' initial mass transfer characteristics with no reaction involved. The AAI is thus a relative measure of the penetration rate [14,15].

1.2.6. Attrition Resistance

Attrition is commonly defined as undesired particle breakage, sometimes as erosive wear, i.e., a superficial size reduction process in a sheared environment [16].

Particle-particle and particle-wall collisions [17] are the primary causes of particle breakage in fluidized beds. Shape matters since more spherical particles will suffer less attrition.

The cycles of cracking and regeneration at high flow rates and temperatures, especially in the riser reactor and cyclones, tend to grind catalyst particles down into micron-sized dust called "fines" [18]. These fines have diameters below $20\ \mu\text{m}$ compared to the average diameter of the catalyst particles, namely 60 to about $100\ \mu\text{m}$. Most FCCUs have fines recovery systems, such as Third Stage Separator (TSS) or Electrostatic Precipitator (ESP), to control the loss of fines to the environment. Attrition resistance is a fundamental parameter in determining the unit retention of catalysts and, accordingly, their cost efficiency.

The attrition index determination procedure is described in ASTM D5757-11 (2017) Standard Test Method for Determination of Attrition of FCC Catalysts by Air Jet. In the test method, the sample is subjected to vigorous fluidization by a constant high-flow air stream, which causes shear and breakage of the particles that collide at high speed with each other and with the walls of the test tube. The fines formed are removed from the attrition zone by elutriation, collected in an extraction cartridge, and weighed after 5 and 20 h of testing, and the attrition is calculated by dividing these values by the initial mass of the catalyst.

2. Objective

This work reviews the literature on FCC catalyst accessibility and how to increase it. This feature is a rough indication of the transport phenomena involved in heterogeneous catalysis, namely the diffusion of reacting molecules adsorbed on the catalyst surface within its pores, adsorption of reactants on the active (acid) sites, desorption of products and their diffusion through the catalyst pores to its surface, with no regard to the reaction step.

High accessibility FCC catalysts are specially designed to promote bottoms upgrade reactions, i.e., conversion of large or bulky molecules present in the heavier fractions of gas oil feed. These molecules must diffuse into the catalyst through macro- and mesopores and crack over alumina to access zeolite micropores and, ultimately, the acid sites in its interior [19,20].

Although catalyst performance correlates well with its specific area, high SA figures do not guarantee high activity. The most significant contribution to SA comes from zeolite. However, if the feed's heavy molecules cannot reach the zeolitic acid sites inside the catalyst, they will not be available for reaction.

Roughly speaking, accessibility can increase by modifications in the binding system, pore system engineering, thermochemical modifications in the zeolite to introduce mesopores, or a higher amount of (mesoporous) alumina in the formulation, to name a few.

3. Methodology of Literature Search

3.1. Search Universe

FCC catalyst manufacture is a mature technology, but there has been room for innovations in recent decades. The search was restrained to the past 30 years, starting in 1990. This timeframe covers a period of inventions and technology development of major catalyst manufacturers as well as new entrants.

Queries were divided into 5-year clusters from 1 January 1990 to 31 December 2020.

3.2. Keywords Selection

As the title suggests, “FCC catalyst” and “accessibility” are the natural choices of keywords. To make the search more comprehensive, some variations have been tried:

- removing the acronym FCC by substituting fluid-cracking catalyst for FCC catalyst;
- using an alias for accessibility, such as porosity and pore size distribution.

Queries were run with the entries above and their combinations, as described in the search strategy.

3.3. Database Selection

During 30 years of search, many technologies of catalyst manufacture and methods to increase accessibility have been studied, developed, and patented.

Most relevant literature on FCC catalysts can be found among Elsevier publications. Scientific papers and books were searched in Scopus and Science Direct databases.

The patent search was carried out in the three major patent databases:

- United States Patent and Trademark Office (USPTO, <https://www.uspto.gov/>, (accessed on 24 May 2021)) for patents filed in the USA.
- European Patent Office—Espacenet (<https://www.epo.org/>, accessed on 24 May 2021)), for those filed in the European Union (EU) countries.
- World Intellectual Property Organization—WIPO (<https://www.wipo.int/>, accessed on 23 May 2021), using the Patentscope Portal for patents applied under the international Patent Cooperation Treaty (PCT).

3.4. Search Strategy

The following steps were followed for the literature search in Science Direct:

1. The entries employed in the basic queries were defining terms “FCC catalyst” and “fluid-cracking catalyst”.
2. Starting in 1990, the search was performed in six 5-year clusters over the 30-year (1990–2020) period.
3. The bibliographic data search was repeated with the keywords for each 5-year cluster.
4. The output was exported as a .ris file.
5. Mendeley Desktop application was used to manage the results, gathering them in the .ris file, from which a spreadsheet was generated in MS Excel© with .xml data.
6. Duplicate articles were removed based on their respective DOI identifiers, thus yielding the results under the column # Articles in Table 1.
7. Refining Terms “porosity”, “pore size distribution”, and accessibility were added to restrain the search. Results are reported under column # Refined in.

8. After reading the abstracts, the # Selected publications category was created, which was the basis for the present work.

Table 1. Science Direct results.

Keywords	# Articles	Refining Terms	# Refined	# Selected
FCC catalyst	2620	porosity	499	110
		pore size distribution	329	66
		accessibility	500	52
fluid-cracking catalyst	470	porosity	125	5
		pore size distribution	51	5
		accessibility	69	2
Total	3090		1573	240

the amount of (Articles, Refined, Selected) terms.

A similar strategy was used when searching for patents, and repeated findings were sorted out by the patent title and selected after reading the abstracts.

3.5. Bibliometric Results

The search in Science Direct base resulted in 23,166 articles, of which 20,076 replicates were discarded. The 3090 remaining articles were narrowed down to 1573 with the Refining Terms “porosity”, “pore size distribution”, and “accessibility”. Title and abstract selection yielded 240 relevant titles.

As the search was extended to cover 40 years of publications, it became clear that the term “accessibility” was not used as a keyword and yielded no results in the period 1980–1989. This finding corroborates our choice to restrain the search universe to 30 years starting in 1990. Only seven relevant articles about pore size distribution or an indirect mention of “accessibility” (but not the keyword) were found.

The first mention of “accessibility” in the literature dates to 1992 [4], referring to the acid sites in the Y zeolite micropore framework. The term has also been acknowledged by Mitchell et al. [1] as essential for FCC conversion.

3.5.1. Articles

The articles retrieved with the Refining Terms are distributed in time, as shown in Figure 3. In the first half of the search universe, less than 200 titles were found in each 5-year cluster, but this number increased in the following periods, exceeding 300 in the past ten years.

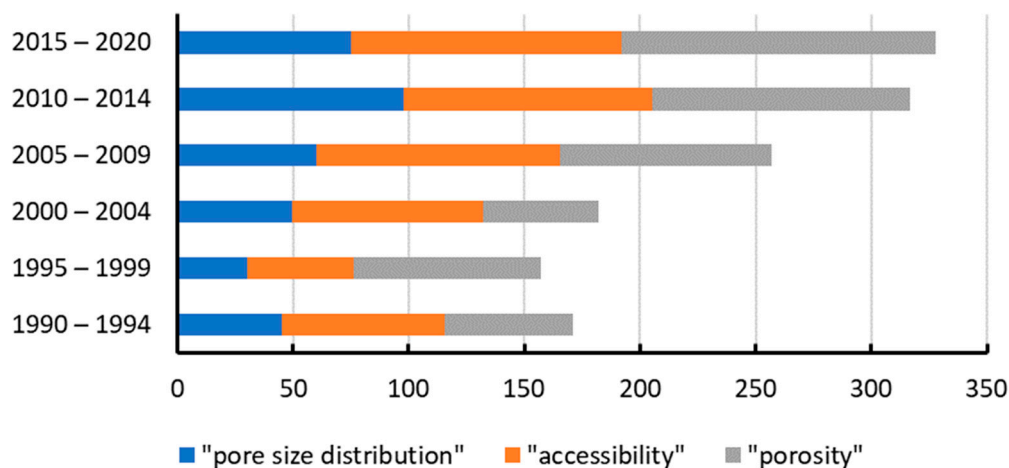


Figure 3. Articles retrieved with the Refining Terms distributed in 5-year clusters.

Noticeably, not more than 240 articles dealing with the Refining Terms were found in the past 30 years (Table 1). Only 54 articles on “accessibility” were considered relevant in the period 1990–2020, which indicates there is room for more investigation on this subject.

Selected publications were found in 64 journal articles and book sections in a non-uniform distribution: only ten journals concentrated 174 articles (72.5% of the total amount), as depicted in Figure 4.

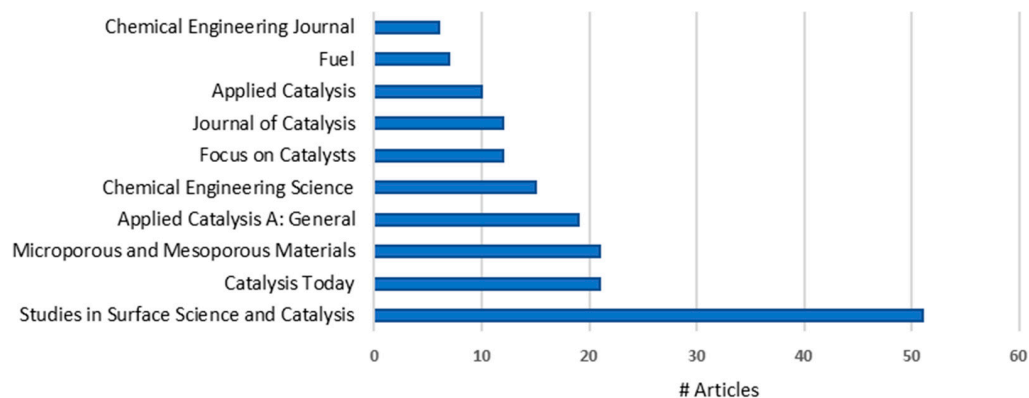


Figure 4. Number of articles published in top ten journals 1990–2020.

A similar search was made using the Scopus database, resulting in Table 2.

Table 2. Scopus results from 1990 to 2020.

Keywords	# Articles	Refining Terms	# Refined	# Selected
FCC catalyst	1694	porosity	53	25
		pore size distribution	17	11
		accessibility	54	18
fluid-cracking catalyst	137	porosity	10	3
		pore size distribution	4	2
		accessibility	3	3
Total	1831		141	62

the amount of (Articles, Refined, Selected) terms.

3.5.2. Patents

The total number of patents retrieved using the keywords in the past 30 years is much smaller than the number of articles. The results of each platform, USPTO, WIPO, and EPO were grouped by keywords, irrespective of the year the patent was published.

Combining the keywords “FCC catalyst” with the Refining Terms yielded more than 85% of the results in each platform, whereas “fluid cracking catalyst” accounted for the rest. After reading the abstract, the most relevant documents were retrieved.

3.5.3. USPTO

USPTO leads the number of selected patents (74%), followed by WIPO (19%) and EPO (7%), as shown in Tables 3–5. A significant number of patents are deposited both in the USA and under the PCT. USPTO documents were kept, and PCT replicates were eliminated.

3.5.4. WIPO

Only PCT deposits were considered in WIPO results to avoid a double count of individual country deposits.

Table 3. Patent search results in the USPTO platform.

Keywords	# Patents	Refining Terms	# Refined	# Selected
FCC catalyst	1319	porosity	176	68
		pore size distribution	122	37
		accessibility	85	3
fluid-cracking catalyst	183	porosity	34	2
		pore size distribution	6	0
		accessibility	13	0

the amount of (Patents, Refined, Selected) terms.

Table 4. Patent search results in the WIPO platform.

Keywords	# Patents	Refining Terms	# Refined	# Selected
FCC catalyst	838	porosity	135	8
		pore size distribution	99	6
		accessibility	187	6
fluid-cracking catalyst	167	porosity	33	3
		pore size distribution	12	2
		accessibility	25	3

the amount of (Patents, Refined, Selected) terms.

Table 5. Patent search results in the EPO platform.

Keywords	# Patents	Refining Terms	# Refined	# Selected
FCC catalyst	3342	porosity	349	5
		pore size distribution	294	2
		accessibility	184	2
fluid-cracking catalyst	330	porosity	61	1
		pore size distribution	23	1
		accessibility	21	0

the amount of (Patents, Refined, Selected) terms.

3.5.5. EPO

Many patents found at the European Office are also deposited under PCT, including those deposited in non-European countries. Similarly, duplicate titles were excluded.

4. Discussion

4.1. Heterogeneous Catalytic Reactions

Fogler [21] describes a sequence of steps involved in heterogeneous catalysis, as depicted in Figure 5. Mass transfer begins with the transport of reactants from the bulk fluid phase onto the external surface of the particle. The molecules then diffuse from the pore mouth to the internal surface of the particles and adsorb on the pore walls. The reaction will only occur on the active sites within the pores, from which the products will desorb and begin their output diffusion path to the pore mouth, from where they will diffuse to the bulk fluid. The rate of the slowest step in the sequence limits the overall reaction rate.

4.2. Diffusion in Solid Heterogeneous Catalysts

When the diffusion steps 1, 2, 6, and 7 in Figure 5 (adapted from [21]) are quick compared with the surface reaction-rate steps (3, 4, and 5), the concentrations close to the active sites are indistinguishable from those in the bulk fluid. In this situation, the transport or diffusion steps do not affect the overall rate of the reaction [21].

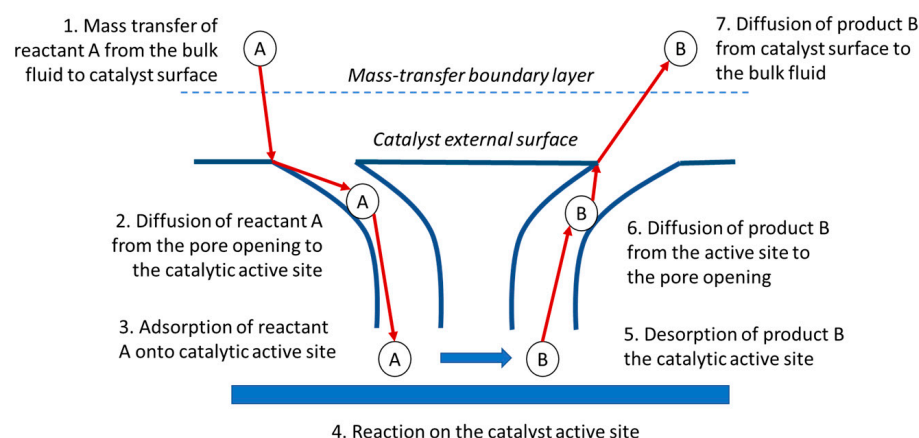


Figure 5. Steps in a Heterogeneous Catalytic Reaction [21].

Mass transport will affect the reaction rate if the reaction steps are very fast compared to the diffusion steps. In systems where the reaction rate is affected by mass transfer (diffusion) from the bulk fluid to the external catalyst surface through the boundary layer, the change in flow conditions around the catalyst will cause the boundary layer thickness to change, with consequences on the overall reaction rate.

Once inside the catalyst, diffusion within the catalyst pores may limit the rate of reaction, and, as a result, the overall rate will not be affected by the external flow regime but by internal diffusion.

Textural characterization provides valuable information to understand the diffusion mechanism within the catalyst. Some parameters such as specific area, pore volume, particle specific gravity, porosity, and tortuosity are involved in diffusion. IUPAC (International Union of Pure and Applied Chemistry) [22] establishes a classification for porous materials: pore shape and pore diameter. As for the pore diameter, IUPAC proposes the classification shown in Table 6.

Table 6. IUPAC pore size classification.

Class	Range of Pore Sizes (nm)
Micropores	<2
Mesopores	2–50
Macropores	>50

4.3. The Importance of Diffusivity in FCC Catalysts

Among the challenges for the catalyst, one may highlight the eventual transport limitation of feed to be cracked into products within the catalyst. The diffusion of feed molecules into the catalyst depends on their size [23]: the larger they are, the more difficult it is for them to diffuse into the catalyst pores. Large feed molecules cannot readily enter the zeolite Y super cage (12.5 Å), the opening of which is only 7.4 Å in diameter [24]. These large molecules must first be cracked on the matrix surface [25].

Catalytic hydrocarbon cracking reactions require strong Brønsted acid sites [26]. Steaming, i.e., treatment with high-temperature water vapor, strongly affects the activity of Y zeolite. A proper steaming of Y zeolite could enhance the cracking activity by over two orders of magnitude. However, excessive steaming leads to a decline in activity from the optimal value.

Zeolite Diffusion

In zeolite-catalyzed processes, limitations imposed by the low, fixed rate of intracrystalline micropore diffusion can remarkably affect catalyst performance [27]. Introducing meso- or macropores may be beneficial for the catalytic performance, i.e., the overall con-

version and the selectivity towards desired products. Additionally, the diffusion path of reactants is reduced, and the accessibility to the active sites is enhanced, which extends the catalyst's lifetime.

Steaming of the zeolite generates cracks, fissures, mesopores, and other defects. These lead to a substantially larger effective external area for diffusion, which then leads to a considerable enhancement in the observed activity. However, steaming also generates non-framework alumina and silica-alumina debris that may block the micropores or the active sites, attenuating the enhancement effect.

In reactions dominated by the monomolecular mechanism, the turnover frequency and the intrinsic activation energy for cracking are practically unchanged by steaming [26]. This observation applies to USY of high SAR because the acidic strength increases when the number of nearest neighbor sites (so-called NNN sites) decreases and almost all acid sites are isolated.

However, a much more significant difference in activity can be observed under conditions where bimolecular and oligomeric cracking dominate. Thus, the phenomenon of enhanced activity by steaming can be explained by the possibility that the bimolecular and oligomeric cracking reactions are pore-diffusion limited.

Falabella et al. [28] have studied the cracking of 1,3,5-triisopropylbenzene (1,3,5-TIPB) over several zeolites with different degrees of dealumination in a differential fixed-bed gas phase plug flow reactor. The 1,3,5-TIPB is a relatively bulky molecule (Figure 6) with a critical molecular diameter of about 9.5 Å. Due to its large size, it has been used to simulate the diffusional constraints expected in the catalytic cracking of gas oil. The authors pointed out that small zeolite crystals (0.8 µm) have at 370 °C a higher 1,3,5-TIPB conversion than the larger zeolite crystals (1.6 µm). They inferred that this behavior was due to the change in the zeolite external area. The authors concluded that when bulky molecules are used, the effect of the formation of mesopores, hence, the increase in external area (mSA), is capital for diffusion-limited reactions.

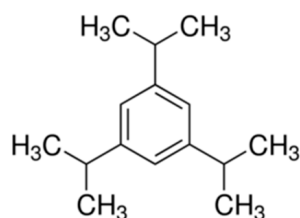


Figure 6. 1,3,5-Triisopropyl benzene molecule.

Product molecules that have been formed by pre-cracking are small enough to enter the zeolite's microporous structure, where they are selectively cracked to naphtha. Various residue feeds, however, have different molecular shapes and will behave differently on the catalyst. Molecules in an aromatic residue are bulkier than those in a paraffinic residue [29]. As a result, it is important to match the pore structure of the catalyst with the molecular size of the residue feed used, which will influence the accessibility to the active sites on the matrix. For a short contact time residue catalyst, the accessibility to the acidic sites and the density of these sites is crucial. Andersson [29] points out that most of the pre-cracking of the large feed molecules takes place on the mesopores area of the catalyst. Moreover, it is also necessary to have some areas in the macropores for cracking the bulky metal-containing feed molecules.

4.4. Hierarchical Materials

According to the Oxford Learner's Dictionary of Academic English, a hierarchy (from the Greek *ἱεραρχία*, *hierarkhia*, "rule of a high priest") is "a system, especially in a society or an organization, in which people are organized into different levels of importance from highest to lowest." Hierarchy is an important and ubiquitous concept in nature, e.g., the leaves and elements of a plant's root system or the blood vessels in the circulatory system:

follow a hierarchical arrangement to optimize structural strength or fluid transport (flow). A wide variety of fields are also hierarchically ordered, such as sociology, business, and military, to name a few [30].

The concept of hierarchy also applies to porous materials, especially zeolitic catalysts, such as the one used in an FCCU. As stated in the previous section, diffusion along zeolite native microporosity occurs at a fixed rate, and another (hierarchically superior) level of pores—intracrystalline or interparticle—is needed to increase mass transfer [31].

Hierarchically porous materials can be classified into two types, depending on the interconnectivity pattern among the different pore levels [32–34]:

- Hierarchy-type I: Interconnected pore system, in which wide pores subdivide into pores of a next lower level (narrower pores).
- Hierarchy-type II: Interconnected systems of pores with different widths in which the wide-pore system intersects the narrower pore system, i.e., small pores branch off from a continuous large pore.

Conceptually, one can consider two approaches to obtaining zeolites with accessible sites. The first one is to create paths from the external surface of the zeolite crystal to the bulk (such as the formation of mesopores). The second is to obtain zeolites with a high external area (such as 2-D zeolite slabs and colloidal zeolites). The latter type of zeolites can still pack together in a way that the inter-crystal space is wide and connected to the external surface of the final grain.

The preparation of zeolites containing more than one system of pores has received many reviews in the literature [33–36]. This material has been generally referred to as hierarchical zeolite [30,37–39]. The preparation methods can be classified into two types. In the first type, the microporous structures are built simultaneously with the mesoporous support or upon this substrate. This method is also referred to as the bottom-up method. In the second type, a microporous solid is first formed and then mesopores are created by subsequent treatments. This second method is referred to as the top-down method.

The bottom-up synthesis method usually employs one or more Structure Directing Agents (SDA), sometimes called porogen materials or templates. These SDAs are termed “hard templates” when they are just physical spacing agents such as carbon, organic, and inorganic polymeric spheres or networks that are added to a zeolite crystallization reaction mixture but do not participate in the zeolitization reactions. After successful zeolite formation, the SDAs are removed by calcination or alkaline-acid leaching, leaving behind mesopores in their former position. By contrast, there are “soft templates”, chiefly Organic SDAs (OSDAs) derived from those employed to synthesize mesoporous silica-alumina, such as poly-quaternary ammonium surfactants. However, when these OSDAs are used alone, they generally only result in materials with amorphous walls. Hence, they are employed together with [33,34,36]:

- Another OSDA that can generate a microporous structure, or
- Seeds of a microporous structure, or
- Functionalization of the substrate structure, such as the attachment of a group that can help generate a microporous structure.

The main drawback of the bottom-up method is the need to use OSDAs. Not only are OSDAs generally expensive or toxic, but their removal also adds further costs and waste treatment steps to the preparation process. Moreover, removal steps such as calcination or acid-base leaching may damage the structure prepared or alter the active sites of the catalytic reaction. More recently, some successful attempts have been reported in the literature making use of the synthesis conditions that promote the intergrowth of two separate yet related zeolite structures (such as FAU and EMT). Consequently, mesoporous spacing is created between crystallites without the use of a template. However, the generalization of this strategy to prepare various structures cannot be assured [40].

Top-down methods are post-treatment methods [33,36]. Synthesized zeolites go through individual or combined acid, base, and heat treatments to generate a system

of secondary pores. The acid treatment, often combined with heat treatment, has been known and employed by the industry for a long time [35,41,42]. Works devoted to the preparation and characterization of zeolites, especially of FAU structure, subjected to these treatments have been widely reviewed. Noteworthy is that as silica is the major component of a zeolite, typical acid treatments will remove the Al in the zeolite framework and will not result in large amounts of mesopores. Furthermore, as Al sites are generally the active sites of a catalytic reaction, the activity of the derived zeolite decreases. Hence, recent works tend to focus on the alkaline treatment of zeolites.

The action of dilute caustic solution on high silica zeolites such as ZSM-5 to generate significant mesopores was published by Ogura et al. in 2000 [43]. Since then, this method has been successfully extended to numerous zeolite structures such as BEA, MOR, and FER [33–35]. Due to its simplicity, flexibility, low cost, and scalability, it has received extensive attention both in academic and industrial communities. The preparation of meso-Y still is more complicated and can be seen in a few examples [31,44].

Patent US 2010/0196263A1 [45] teaches that mesoporous Y zeolite can be prepared following a sequence of acid and alkaline treatments. The authors claim to have introduced controlled mesoporosity with high yield in low Si/Al Y zeolites without losing crystallinity. Mesopores formation proceeds possibly through a surfactant-assisted crystal rearrangement mechanism. Under basic conditions, some Si-O-Si bonds are broken to offer some flexibility in the crystalline structure and yield negatively charged sites in the zeolite framework that attract cationic surfactants. Electrostatic interactions between the negatively charged sites and the positively charged surfactants and the self-assembly of surfactant cations to form micelles within the zeolite crystals cause the crystal structure to rearrange to form mesopores around the micelles.

Compared with equilibrium catalysts (e-cats), the catalysts prepared with mesoporous zeolite improved coke and bottoms conversion and increased LCO and gasoline yields [44].

Pérez-Ramírez et al. [31,46] introduced mesopores in Y zeolites with different Si/Al, following a dealumination/desilication sequence with acid and alkaline leaching. Acid (H_4EDTA and Na_2H_2EDTA) and base (NaOH) treatments have increased mSA up to $500\text{ m}^2/\text{g}$ while preserving the intrinsic zeolite properties. Mesoporous Y zeolite catalytic test in a MAT unit showed increased bottoms conversion and improved product selectivity compared to conventional catalyst with similar activity, better quality diesel, and LPG.

4.5. The Concept of Accessibility

O'Connor [23] defines the term accessibility by asserting that catalyst sites are accessible if they can be reached by the compounds that are supposed to interact with these sites within a given time limitation as set by the catalytic process.

The role of the mass transfer rate of hydrocarbons into the catalyst and of products out of it gains importance as contact times between catalyst particles and feed molecules in the FCCU turn shorter.

O'Connor et al. [47] revealed a proprietary method to characterize catalyst accessibility based on the non-steady state diffusion of hydrocarbons into FCC particles. This technique can be used to quantify catalyst accessibility and optimize catalyst effectiveness in an FCCU operation. They have observed a significant loss of accessibility quantified by an Albemarle Accessibility Index (AAI) as a function of catalyst age and metal content.

The rapid loss of AAI in the e-cats with metals and coke laydown was investigated. Only the catalysts with a high fresh AAI could retain an acceptable value with the aging time, although all catalysts are affected by this phenomenon.

Diffusion of the larger reactant molecules through the catalyst's porous structure to the reaction sites can be a significant factor to determine the overall reaction rate.

To improve bottom upgrading performance, many catalysts have high alumina matrices, which are more resistant to the severe deactivation conditions of the commercial operation, with temperatures about $700\text{ }^\circ\text{C}$ or higher and steam in the regenerator. The hurdles in the mass transfer of large molecules through the catalyst pores and the higher

content of contaminant metals, such as Ni, V, and Fe, are inherent to heavier feedstocks [48]. The pore systems of these materials, then, are to play a crucial role in assisting mass transfer processes. Figure 7 (adapted from Vogt et al. [3]) schematically depicts the pore system in FCC catalysts.

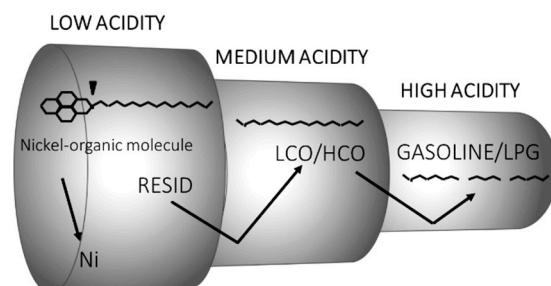


Figure 7. Pore hierarchy in an FCC catalyst.

The pores with different sizes are arranged in the ideal hierarchy, with the larger pore meeting the large molecules first. Furthermore, the distribution of acid sites should be aligned with pores of different accessibility. Narrow pores and high acidity are needed to crack small hydrocarbon molecules; conversely, bulkier molecules can be cracked in wider pores, whose acidity is lower.

4.5.1. Meso-Chemistry—A New Area of Investigation

In recent years there has been an interest in nanotechnology, where the control of events is in the atomic or molecular scale [30,37–39]. However, concerning reactions over an FCC catalyst, reactants must diffuse through a path length of 10 to 40,000 nm to reach the active sites and undergo cracking.

Noteworthy effects and functionalities that are important in macroscopic phenomena begin to manifest themselves and cannot be described only by laws of the atoms and molecules scale alone. This range can be named the mesoscale, and it works as a bridge between the nanoscale and the macroscale.

Consider the consecutive reaction $A \rightarrow B \rightarrow C$.

In nanoscale chemistry: For a given type of catalyst site, the distribution of products B and C (selectivity) is controlled by the extent of the reaction.

In mesoscale chemistry: product selectivity is also controlled by the catalyst's accessibility. If Catalyst 1 and Catalyst 2 have the same type of active sites, but different accessibility, they will yield different product distributions at the same degree of conversion of A. This is a usual phenomenon in FCC.

Accessibility is intrinsically affected by pore connectivity and tortuosity. Connectivity can be defined as the number of pores intersecting at a node [49]. The pore system in an FCC catalyst particle forms a network of pores that intersects in nodes and connects to each other and to the particle's surface.

Two particles may have the same pore size distribution and still different accessibilities. During a reaction, the reactant can reach the active site of one catalyst in a shorter time than the other, i.e., one catalyst can be more accessible than the other if the time spent for the reactant to reach the catalyst sites—and products to leave—is shorter. The origin of the improved performance is directly linked to the existence of interconnected networks of micro- and mesopores [50]. This comparison has important catalytic consequences, not only on the reaction rate but also on the selectivity of more complex reactions and further on the catalyst deactivation and life.

The direct participation of macro- and mesopores in the kinetics of adsorption indicates that their role in facilitating molecular diffusion is more substantial than shortening the micropores' diffusion path.

4.5.2. Characterization of Accessibility

Although physical properties such as mesoporosity have been recognized as important, little significant attention has been paid to the influence of mass transfer barriers caused by various manufacturing processes and those induced by a few contaminants in the performance of FCC catalysts. Such barriers are significant in short contact time FCCU [4].

Nitrogen or argon physisorption and mercury penetration porosimetry are employed to obtain average textural properties and pore size distribution (PoSD) but offer limited information on pore connectivity. Three-dimensional (3D) information from X-ray Micro-Computed Tomography (μ -CT) or Electron Tomography (ET) can determine the structural parameters and help visualize the porous structure [51,52].

Figure 8 is a 3D reconstruction of an X-ray μ -CT image showing interconnected, isolated, and surface-bound porosity in a catalyst control volume (model developed by the author with the use of artificial intelligence tools (Bing Image Creator), [53]). The more the main network of pores connects to the catalyst surface porosity, the higher the connectivity (and accessibility).

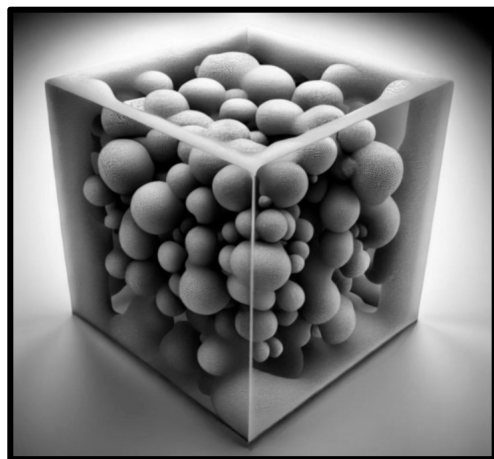


Figure 8. Three-dimensional micro-CT reconstruction model of a porous catalyst sample showing pore connectivity.

Other methods to assess pore connectivity include NMR cryodiffusometry, hyperpolarized ^{129}Xe NMR, and Small-Angle X-ray Scattering (SAXS), to name a few:

- Cryoporometry (thermoporometry) is a technique used to determine pore size distributions of solids. It is based upon the phenomenon that the melting or freezing point of a fluid imbibed within a porous solid is depressed below that of the bulk solid by an amount inversely proportional to pore size [54]. Water, cyclohexane, and benzene are common probe fluids used in cryoporometry: their choice is limited by criteria such as the requirement that no part of the sample be soluble in the probe fluid. The cryoporometry technique can be performed using either NMR spectroscopy (NMR cryodiffusometry) or calorimetry.
- ^{129}Xe NMR allows probing pore sizes and pore connectivity or pore-blocking. These parameters make the technique particularly interesting for investigating hierarchical functional materials on different length scales. Obtaining sufficient signal intensity in a reasonable experimental time remains a limitation of the method, which can be overcome by hyperpolarization techniques [55].
- 3D imaging in a transmission electron microscope is called electron tomography (ET). Transmission images of the sample acquired from at least a hundred different angles can be reconstructed into a 3D model of the sample. This technique has a very high resolution (tens of nanometers) but is only suitable for tiny samples [56].
- Computed tomography (CT) is a non-destructive 3D imaging technique based on the different X-ray attenuation of materials. Its non-destructive nature allows temporal

investigation (4D imaging, where the fourth dimension is time), and the examined samples remain unchanged, can be further investigated (even in situ), or can be used. Virtually no sample preparation is required. The main limitations of CT are related to the high Z (atomic number) contrast necessary for good imaging quality. Low-Z materials and samples with low X-ray attenuation contrast are challenging to measure, whereas very high Z materials (e.g., metals) can introduce severe artifacts and worsen image quality. Micro-CT (μ -CT) stands for high-resolution CT. With the decrease in focal spot size and increased resolution, developers could achieve submicron resolution and started referring to devices capable of this high resolution as nano-CT. After some time, with the use of synchrotron radiation and special X-ray optics, even better resolution (below 100 nm) became obtainable [56].

- Small-angle X-rays scattering (SAXS) technique uses X-ray beams to penetrate the materials and obtain information on the pore structure by measuring the intensity of scattered radiation within a specific range of scattering angles (0.1 to 5°). It is a non-destructive measurement of the total porosity, including both open and closed pores, providing information on pores from angstrom to micron scales (from ca. 5 \AA to $20 \text{ }\mu\text{m}$) [57]. In mercury porosimetry, the lower limit of the detectable pore throat is approximately 3 nm , whereas the helium pycnometry method can obtain gas-accessible porosity but not total porosity; the SAXS method, on its part, includes both accessible (open) and inaccessible (closed) porosity—although this is not a relevant information for catalytical purposes.

4.5.3. Accessibility Effect on Catalytic Performance: Relevance to FCC On the Rate of Reaction

The nature of the porous structure of the catalyst particle should be examined closely because diffusion to and from the catalytic sites is essential in determining the overall reaction rate. Materials and methods of catalyst manufacturing can dramatically affect the porous structure. In addition to the distribution of pore sizes, their shape can also be relevant [4]. Aside from the idealized arrangement of pores presented in Figure 7, for the reactants to reach the interior of the catalyst particle they must pass through the surface, so diffusional restrictions must be minimized in the boundary layer.

On the Reaction Selectivity

The importance of diffusion for a simple reaction has been presented in previous sections. In the FCC process, the reactions to consider are more complex since the cracking of heavy molecules of the feed will undergo further reactions.

Hence, the immediate observation is that reaction products must diffuse out of the catalyst particle quickly enough to prevent overcracking to unwanted light products.

Coke and heavy metals deposition on the FCC catalyst can cause fouling and pore-mouth plugging. Fouling can change pore architecture and cause significant differences in catalyst selectivity, whereas pore plugging reduces the accessibility of the catalyst matrix.

Furthermore, we could generalize and consider the effect of accessibility on the selectivity of sequential reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, where k_1 and k_2 are catalytic reaction-rate constants. In the absence of diffusional resistance, the ratio of the reaction-rate constants gives an intrinsic yield. On the other hand, if the two consecutive reactions are highly influenced by diffusional resistances, there will be a remarkable yield reduction.

On the Catalyst Acidity

The relationship between acidity and accessibility should be discussed with different approaches, namely at the catalyst-preparation level (ingredients and compounding) and the catalyst application.

- At the ingredient level: Zeolite micropores pose the main restriction to diffusion in a catalyst, and the ways to increase it belong to the nanoscale manipulation. Soft or hard templates can be added to the zeolite synthesis to introduce mesopores, thus

increasing accessibility to the zeolite active (acid) sites located in the framework (bottom-up methods). Virtually the same framework composition as the strictly microporous reference zeolite can be obtained; hence, the mesoporous zeolite will bear the same acidity in terms of number and strength as the reference material.

Top-down methods, on the other hand, create mesopores at the cost of micropores destruction. They involve dealumination or desilication. In both cases, acidity will change, reflecting the framework composition change (higher or lower SAR).

- At the catalyst assembling level: A more accessible zeolite does not mean a more accessible catalyst. It is useless to embed a hierarchical zeolite if the large molecules of the feed cannot reach the crystal. The key to accessibility increase lies in the compounding technology, the way the ingredients are packed, arranged, and bound in the catalyst particle. Here we deal with mesoscale phenomena, in which the extent of macroscale mass transfer within the catalyst pore network will change the product yield and selectivity.
- During catalyst application/operation: Calcium and heavy metals contaminants (iron, nickel, vanadium) present in crude oils as porphyrins, naphthenates, or inorganic compounds can deposit on the FCC catalyst surface during cracking and destroy the crystalline structure, block pore channels, and cover the catalyst's active sites. The catalyst's selectivity and activity decrease, and coke and dry gas yield are higher with a simultaneous decrease in liquid fuel yield [58].

Yuxia et al. [58] have impregnated FCC catalysts with two kinds of iron (Fe) species (iron chloride and iron naphthenate) to simulate contamination sources from FCC feedstocks. Fresh FCC catalyst and Fe-contaminated samples were steam-deactivated, and their performance was carried out on an ACE unit.

The contamination of iron chloride showed little influence on the catalyst performance, while the activity of the catalyst contaminated with iron naphthenate decreased with increasing iron content.

Scanning Electron Microscopy with Energy Dispersive X-ray Analysis (SEM-EDAX) revealed that the distribution of iron on the surface of the catalyst contaminated with iron chloride is uniform, and the Fe contents in the exterior and interior of the catalyst particles are close, suggesting the absence of local enrichment of Fe deposits. The catalyst contaminated using iron naphthenate presented a non-uniform iron distribution, with the Fe content in the exterior of the FCC particle markedly higher than that in its interior.

The total acidity of the Fe-contaminated samples was measured with NH_3 -TPD methods, and the results were compared with the fresh catalysts. The authors noticed significant acidity loss in Fe naphthenate-contaminated catalysts and that acidity loss is negligible when Fe chloride is used.

On the Catalyst Life

Various contaminants are less widely recognized and studied regarding their effects on the FCC process. Fe and Ca probably have little inherent catalytic activity but have been associated with surface deposits that clearly could have a significant impact on the access to the interior of an FCC catalyst particle [33].

Weckhuysen et al. [3,59,60] characterized commercial e-cats and artificially deactivated and metalated catalysts using the techniques of X-ray micro- and nano-tomography, as well as μ -XRF and μ -XRD. They have concluded that both contaminant metals Fe and Ni gradually incorporate almost exclusively near the external surface regions of the FCC catalyst particles in a shell not thicker than 2 μm , represented by the green annulus in Figure 9 (adapted from [59]), thus severely limiting the macropore accessibility as metal concentrations increase.

The authors [59] carried out a catalyst performance test (ACE) on the e-cats with different metal levels using VGO at a cracking temperature of 538 °C and at different catalyst-to-oil (CTO) ratios: 3, 4, 5, and 6. ACE results show a clear correlation between

catalyst deactivation/age (and therefore the levels of Ni and Fe in the sample) and catalytic activity: the older the catalyst, the lower the bottoms conversion.

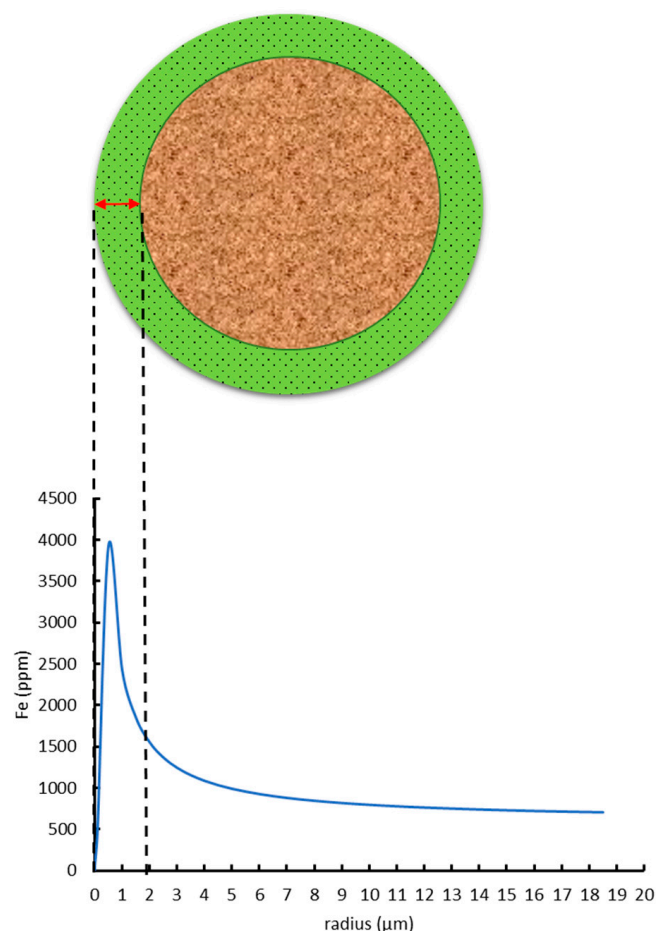


Figure 9. Cross-sectional view of an FCC catalyst particle depicting contaminant metals (Fe, Ni) distribution along its radius. The metals concentrate in the outermost green annular region around the catalyst particle (brown circle).

Pore-blocking prevents feedstock molecules from reaching the catalytically active sites. Consequently, metal deposition reduces the catalytic conversion with increasing time on stream because although the internal pore system remains unobstructed, it becomes mostly inaccessible.

Commercial FCC unit yields are directly related to accessibility. Figures 10 and 11 (adapted from [61], used under permission of Albemarle Co., Charlotte, NC, USA) show the increase in conversion and gasoline yield as the catalyst ages in a commercial FCCU [61].

Nickell [14] has documented commercial cases illustrating a tangible correlation between AAI and unit performance. Figure 12 (adapted from [14], used under permission of Albemarle Co.) shows the decrease in activity (bottoms conversion) as the catalyst ages in the FCCU, with the consequent decrease in accessibility. It is noticeable that the catalyst fell below the refiner's "critical AAI"; a point where the bottoms increased remarkably as the conversion correspondingly decreased.

Empirical observations consistently demonstrate that many refiners experience a "critical accessibility level". This critical level is extremely unit-specific and is a function of feed quality, feed–catalyst contact efficiency, riser residence time, equilibrium catalyst metal levels, and regenerator conditions. Operating with accessibility levels below this point results in significant losses in FCC unit conversion and transportation fuel production. This observation does not show in traditional equilibrium catalyst laboratory testing [61].

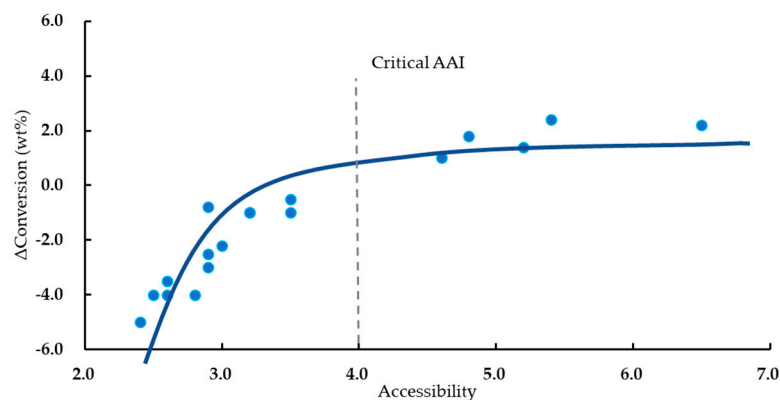


Figure 10. Effect of FCC accessibility on conversion.

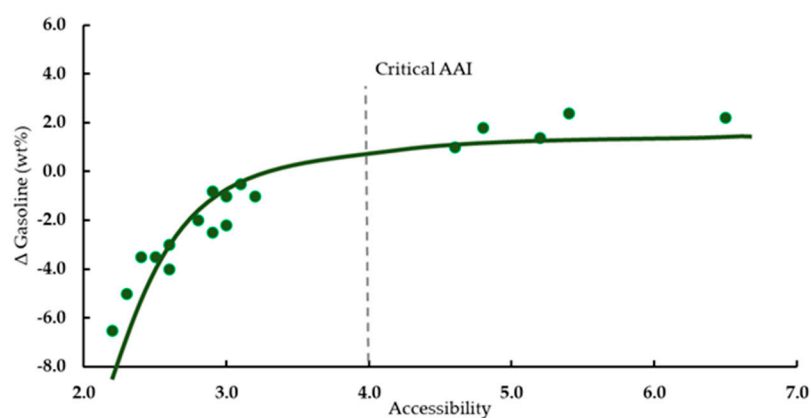


Figure 11. Effect of FCC accessibility on gasoline yield.

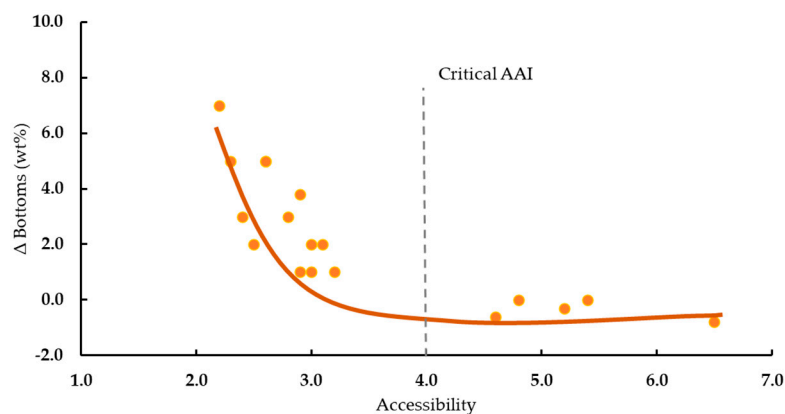


Figure 12. Effect of accessibility on bottoms conversion.

4.6. Attrition Resistance \times Accessibility

FCC catalyst assembly is the art and technique of combining different materials into a single composite designed to have the desired physicochemical characteristics and catalytic performance. The binder surrounds the ingredient particles and holds them together by their contact points [3]. Water—and eventually some other volatile matter—evaporates in the drying process, leaving voids in the interstices of the particles that form a secondary pore system, mainly in the meso- and macro-regions.

As the porosity of the microsphere increases, however, the rate at which it fractures and wears down to finer particles within the FCCU increases, resulting in increased particulate emission from the unit and higher demand for fresh catalyst addition rates. Composition

or processing procedures to reduce the rate at which an FCC catalyst wears for a given total pore volume are of fundamental importance to improve the performance of the catalyst [6].

Pore volume in the micro (<2 nm) range is known to yield increased coke. Mesopores (2–50 nm) play a significant role in catalytic reactions, by improving coke selectivity and macropores (50–1000 nm) will serve as conveyors for bulky reactants, thus enabling short contact reaction times [6].

The increase in mesopore volume is directly related to the higher accessibility. Mesopores ensure optimal accessibility and transport of reactants and products, while zeolite micropores induce the preferred shape-selective properties [62].

The amount of binder is capital for the physical properties of the catalyst, and it should be balanced to account for the best match of accessibility and attrition resistance [11]. Higher binder intake improves the catalyst's mechanical strength (lower AI), but its nanoparticles can fill some of the zeolite micropores rendering them useless for the cracking reactions. Conversely, too little binder is deleterious to adhesion, which increases the attrition index (AI) and causes catalyst losses to be high in the FCCU.

In general, accessibility and mechanical resistance are two desirable features of the catalysts. Nevertheless, in preparation, a parameter that favors one typically disfavors the other. In the next section, we will examine methods of increasing FCC catalyst accessibility but also examine their side effects on other catalyst properties, especially on the mechanical resistance.

4.7. Methods to Increase FCC Catalyst Accessibility

Although the chemistry in the mesoscale is rather complex, attempts to modify the accessibility in the FCC catalyst can be even more challenging since compounding systems are very heterogeneous.

Increasing mesoporosity in the zeolite system belongs to the nanoscale manipulation, and it has been dealt with in many publications in the open literature [31,37,38,63–66]. In contrast, the modification of catalyst pore structures and their connectivity are limited to patent publications. Furthermore, the comparison between these approaches is scanty, and the effects of manipulations are not tackled on a scientific basis.

Accessibility can increase using pore engineering methods, including modifications in the steps of:

- Synthesis or modification of precursors (precipitation, acid/base treatments, hydrothermal processes).
- Drying of the Catalyst Precursor Slurry, by reducing the surface tension of the solvent (soft templating).
- Catalyst compounding, such as ingredients with larger average particle size; aging of the binding species; addition of a solid porogenic agent, which is later removed, and leaves empty spaces in the matrix (hard templating).

Ingredients with larger average particle sizes will contribute only marginally to the increase in accessibility and bear a high risk of increasing the attrition index.

Aging of the binding system through pH change or temperature increase will cause its particles to increase their size faster by polymerization [67], which is ultimately the same effect described above, with the same risks of increasing the attrition index.

In the soft templating strategy, interparticle mesopores can be introduced in the catalyst matrix by the action of surfactant molecules that avoid shrinkage and collapse of the pores during particle formation. A well-known problem is the shrinkage of gels during drying due to the capillary force arising at the hydrophilic surface of the gels and solvent. To minimize the capillary force, modifying sols with organic species renders the surface hydrophobic to prevent shrinkage [68]. In the early drying stage, the gel (matrix) shrinks with the decrease of the liquid volume in the pore. Then, after the liquid leaves the pores, the capillary forces disappear, and the volume of the matrix comes back almost to the same volume as the wet gels (spring back effect), resulting in highly porous xerogels (ambient pressure aerogels).

A variation of the soft templating in FCC catalyst production relies on the addition of species that can be decomposed in the drying step, producing gases that will force their way out of the catalyst and minimize the formation of the hard silica shell.

Hard (or solid) templating techniques use a template or filler (Pore-Regulating Agent, PRA) that remains in the solid state throughout the whole preparation process of the catalyst, after which it can be removed, thus creating large pores. The choice of PRA should consider the following criteria: (i) their surface properties should be compatible with the chemical properties of the ingredients (mainly the binding system), (ii) they should be stable at the compounding conditions (temperature and pH), and (iii) the remaining catalyst structure should be stable after removal of the hard template [30].

The addition of PRAs presents itself as a safer and more efficient way to increase accessibility with little or no damage to Al [69]. In this context, PRAs are defined as additives embedded into an inorganic matrix and afterward washed or burned out to generate meso- and/or macropores. They have been extensively used to control the pore structure of catalyst supports, mainly in the development of hydroprocessing catalysts, which usually require a bimodal distribution with a certain percentage of macropores to allow for the internal diffusion of heavy molecules [69].

Carbon black and crystalline cellulose are the combustible materials most often used as pore generator additives. Other materials such as active carbon, wood flour, sugar, starch, and several polymers have also been reported.

4.8. Pore-Regulating Agents (PRA)

Embedding combustible fillers in inorganic matrices and burning out their carbonaceous matter leaves a void, thus generating pores. A direct correlation, for instance, has been found between carbon black particle diameter and the size of the pores generated. A wide range of PRAs to manufacture fixed-bed catalysts has been reported in the literature (Table 7).

Table 7. Use of pore-regulating agents in extrudates.

Type of PRA	Size Range	References
Carbon black	10 to 100 nm	[70,71]
Active Carbon	Typically > 100 nm	[72]
Wood flour	out of desired range	[73]
Cellulose	10 to 400 nm	[74]
Starch	Not reported	[75]
Sugar	10–100 nm	[69,76]
Organic Polymers	Wide range depending on choice: 10–100 nm, 100–1000 nm	[76]

Pore Size Distribution (PoSD) of FCC catalysts that use silica as the binder is very dependent on the content of each component. Increasing zeolite content leads to an increase in the macropore region, whereas the increase of alumina or silica binders leads to a decrease. In contrast, using these PRAs should allow the control of the PoSD, regardless of FCC catalyst formulation [69].

Even though pore size distribution may not be the ultimate method to compare the accessibility of different catalysts, it can still furnish leads. This is the case when the catalyst-preparation methods provide sufficient connectivity between larger pores, so the diffusion to the external surface of the catalyst is typically governed by parameters such as the mean pore diameter. Two catalysts may have the same mesopore area and almost similar pore size distribution, still, the extension of connectivity can render their accessibilities very much different from one another (Figure 13).

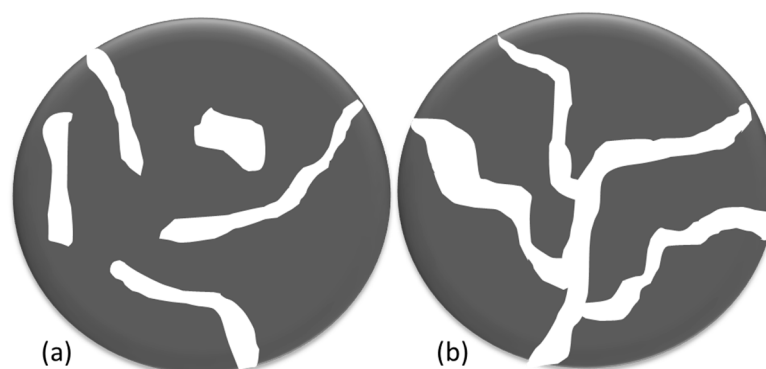


Figure 13. Same porosity, different connectivity. (a) closed and dead-end pores (non-connecting); (b) network of connected pores.

Pores connectivity and their hierarchy are the keys to accessibility. The choice of PRA and the strategy of addition affect connectivity. Typical methods that employ combustible PRAs may give rise to closed or dead-end pores that do not connect to the outer side of the catalyst and lead to the poorest case of accessibility.

If one employs methods such as the decomposition (gasification) of added chemicals, the final structure will most probably contain escape routes for the products of the PRA decomposition, which result in connectivity to the external surface (situation b) instead of (a) in Figure 13.

At any rate, precaution must be taken to ensure that the larger pores formed are connected hierarchically to narrower pores and the catalyst surface.

5. Conclusions

FCC catalyst technology continues to evolve to meet the demands of the refining industry. Opportunity feedstocks such as heavy crudes, bitumen, or unconventional oil yield gas oils present specific challenges to the operation of the FCCU and catalyst formulation. Furthermore, the production objectives may change and depart from the original ones of the unit design.

Large molecules in the feed must diffuse into the catalyst, crack, and be selectively converted on the zeolite acid sites. Similarly, products should desorb and diffuse out of the pores briefly, to avoid secondary reactions or overcracking. In other words, accessibility is the key parameter to control the two-way molecular traffic in and out of the catalyst pore system.

Fundamentally, the accessibility concept rests in increasing FCC catalyst diffusivity so that mass transfer is no longer the rate-determining step of cracking reactions.

It is well known that steam calcination can create mesopores by extracting aluminum atoms from the zeolite framework. Besides crystallinity, micropore volume, and specific area losses, non-framework alumina remains in the pores and is responsible for non-selective reaction pathways.

Patent literature teaches other methods to introduce mesopores while preserving the intrinsic zeolite properties. A family of inventions claims to have increased the mesoporous specific area with surfactant-assisted successive acid and basic treatments. Although effective, introducing new steps can add complexity to the process and increase the cost of production.

Perhaps a more effective and flexible way to introduce or increase accessibility in catalyst formulation is achieved using pore-regulating agents (PRAs) in the compounding step. PRAs are added ex-recipe and affect the behavior of the slurry in the drying step, either mechanically (void-filling) or by changing the surface tension of the aqueous phase. In any case, PRAs can be removed from the catalyst during the (spray-)drying step—or in thermal post-treatment (calcination)—leaving their effect behind.

Extensive literature has been found on using PRAs in fixed-bed catalysts. However, hardly any have been found to increase FCC catalyst accessibility, which shows that it is necessary to study the fundamentals of PRA effects, not only what substances can generate porosity, but how they do it and their effect on attrition resistance.

In addition, methods and techniques to determine accessibility in FCC catalysts must be developed, mainly those in which diffusion and mass transfer parameters are calculated.

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