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EVOLUTION OF FCC CATALYSTS AND SELECTIVITY MECHANISMS: A CONCEPTUAL MODEL BASED ON THE STRUCTURE–ACIDITY–DIFFUSION APPROACH

Shargiya Gasimova, Rahila Huseynova
Baku State University, Baku, Azerbaijan

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Fluid Catalytic Cracking (FCC) is one of the principal conversion processes in modern petroleum refining, enabling the transformation of heavy petroleum fractions into high-octane gasoline and light olefins. The growing global demand for transportation fuels and low-carbon chemical feedstocks requires further optimization of both the efficiency and selectivity of FCC technology. The technological and economic performance of the process is determined directly by the structural properties of the catalysts used, the nature and distribution of acid sites, and the architecture of the pore system.

The historical development of FCC catalysts has been characterized by a transition from natural aluminosilicates to synthetic amorphous systems, and subsequently to zeolite-based catalysts possessing high stability and shape-selective properties. This evolution has not only increased catalytic activity but has also enabled the controlled distribution of products and the optimization of selectivity on a mechanistic basis. In particular, the application of USY and ZSM-5 type zeolites has played a key role in increasing gasoline yield, selectively producing light olefins, and controlling hydrogen transfer reactions.

The primary objective of this study is to systematically analyze the evolutionary stages of FCC catalysts, explain the mechanisms governing selectivity formation within the context of structure–acidity–reaction mechanisms, and substantiate the relationship between catalyst properties and product distribution within a conceptual model framework. For this purpose, the type and density of acid sites, the influence of pore size on diffusion, the carbocation mechanism, and catalyst deactivation factors have been evaluated analytically.

The study is conducted on the basis of systematic literature analysis and theoretical synthesis without performing empirical experiments. The proposed structure–acidity–selectivity model provides a theoretical foundation for future developments in FCC technology, particularly for propylene-oriented processes and the production of environmentally compliant low-emission fuels.

Keywords: catalytic cracking, FCC, zeolite catalysts, selectivity mechanism, pore structure, USY, ZSM-5, catalyst deactivation, product distribution.

INTRODUCTION

Fluid Catalytic Cracking (FCC) remains one of the most important conversion technologies in modern petroleum refining because it enables the transformation of heavy hydrocarbon fractions into high-value products such as gasoline, liquefied petroleum gas,

E-mail address: rahilahuseynova@bsu.edu.az

propylene, and other light olefins [1]. Recent developments show that FCC is no longer viewed only as a gasoline-producing process, but increasingly as a flexible refinery–petrochemical integration platform capable of responding to changing demand for fuels and petrochemical feedstocks [1,2].

The performance of FCC units is determined largely by the physicochemical properties of the catalysts used. In particular, catalyst structure, pore architecture, acidity distribution, diffusion behavior, and resistance to deactivation jointly influence hydrocarbon conversion pathways and product selectivity. Modern FCC catalyst research therefore focuses not only on increasing conversion, but also on controlling selectivity toward desired product fractions through rational catalyst design [1,3].

Zeolite-based catalysts have played a decisive role in the development of FCC technology. The introduction of Y-type and ultrastable Y (USY) zeolites improved gasoline yield and hydrothermal stability, while the use of ZSM-5 additives enabled increased formation of light olefins, especially propylene [1]. More recent studies emphasize the importance of hierarchical zeolite structures, where the combination of micro- and mesoporous channels reduces diffusion limitations and improves accessibility of active acid sites [3,4].

Diffusion control has become one of the central issues in modern FCC catalyst engineering. In conventional microporous zeolites, bulky hydrocarbon molecules may experience transport limitations, which increases residence time inside the catalyst pores and promotes secondary reactions such as hydrogen transfer, aromatization, and coke formation. Hierarchical zeolites address this problem by shortening diffusion pathways and improving molecular transport efficiency [3]. Experimental studies on hierarchical ZSM-5 also show that smaller crystal size and reduced diffusion resistance can improve light olefin selectivity and decrease coke formation [4].

At the same time, the modernization of FCC technology is strongly influenced by broader energy-transition trends. Refineries are increasingly considering renewable and waste-based feedstocks, including biomass-derived oils and recycled carbon streams, as partial substitutes for conventional fossil feedstocks in FCC units [5]. This shift creates new catalyst-design challenges because oxygenated and contaminant-rich feedstocks may intensify coke formation, alter acidity requirements, and accelerate catalyst deactivation [5].

Despite extensive research on FCC catalyst acidity, pore structure, diffusion behavior, and deactivation mechanisms, these factors are often studied separately. However, catalytic selectivity in industrial FCC systems emerges from the combined interaction of these parameters rather than from any single factor alone. Therefore, there is a need for an integrated conceptual framework that links catalyst structure, acidity, diffusion, and time-dependent deactivation into a unified explanation of product selectivity.

The purpose of this study is to analyze the evolution of FCC catalysts and develop a conceptual model explaining catalytic selectivity through the structure–acidity–diffusion–deactivation relationship. The proposed framework interprets FCC selectivity as a multi-parameter response shaped by structural confinement, acid-site accessibility, molecular transport, and catalyst aging processes. This approach provides a theoretical basis for future catalyst-design strategies aimed at optimizinggasoline-oriented, olefin-oriented, and environmentally compatible FCC processes.

THEORETICAL FRAME

Hierarchical Zeolites and Transport-Controlled Selectivity Enhancement

One of the most significant developments in modern FCC catalyst engineering is the introduction of hierarchical zeolite structures combining microporous catalytic domains with secondary mesoporous transport channels. These materials were developed in response to limitations associated with purely microporous zeolites, where restricted molecular mobility increases residence time of bulky intermediates and promotes undesired secondary reactions such as hydrogen transfer and polyaromatic condensation leading to coke formation [6].

Experimental studies demonstrate that hierarchical pore connectivity significantly

improves accessibility of internal Brønsted acid sites and enhances catalytic performance during conversion of vacuum gas oil fractions. In particular, desilication-assisted hierarchical ZSM-5 catalysts exhibit increased external surface area and improved diffusion efficiency without substantial loss of framework acidity, resulting in higher propylene selectivity compared with conventional microporous structures [7].

Similarly, hierarchical USY catalysts prepared through controlled dealumination and mesostructure formation show improved hydrothermal stability and reduced coke deposition during long-term catalytic operation. Electron microscopy investigations confirm that secondary mesoporous networks facilitate removal of reaction intermediates from microporous domains and prevent accumulation of condensation precursors inside zeolite frameworks [8].

Nitrogen adsorption and pore-distribution analyses further indicate that hierarchical catalysts reduce diffusion resistance by increasing effective transport pathways available to large hydrocarbon molecules. As a result, catalytic cracking reactions become less transport-limited and more strongly controlled by intrinsic acid-site activity, leading to improved selectivity stability under industrial FCC operating conditions [9].

These findings support the interpretation that hierarchical pore engineering represents not only a structural modification strategy but also a selectivity-control mechanism capable of regulating intermediate lifetime within catalytic environments.

ZSM-5 Additives and Selective Light Olefin Formation

The incorporation of ZSM-5 zeolites into FCC catalyst formulations represents one of the most effective strategies for increasing light olefin yield in refinery operations. Unlike large-pore zeolites such as USY, the medium-pore MFI framework restricts formation of bulky transition states and suppresses bimolecular hydrogen-transfer reactions responsible for paraffin formation [10].

Kinetic studies demonstrate that the primary mechanism responsible for increased propylene selectivity in ZSM-5-containing catalysts involves enhanced cracking of gasoline-range hydrocarbons into lighter olefin molecules through secondary β-scission pathways. Because the narrow channel structure of ZSM-5 limits formation of polyaromatic intermediates, olefin molecules escape the catalyst pores before undergoing saturation reactions, thereby increasing propylene yield [11].

Recent experimental investigations further show that nano-sized ZSM-5 crystals provide shorter diffusion pathways and higher external surface accessibility compared with conventional microcrystalline materials. This structural modification improves catalytic efficiency during secondary cracking of C_7–C_9 hydrocarbons and enhances selectivity toward propylene and butylene fractions [12].

In addition, the effectiveness of ZSM-5 additives depends strongly on acid-site distribution within the catalyst matrix. Optimized incorporation of ZSM-5 into FCC catalysts enables functional differentiation between primary cracking domains locatedin USY frameworks and secondary olefin-production domains located in MFI structures. Such spatial separation of catalytic functions represents a key principle underlying modern propylene-maximization FCC strategies [13].

Recent refinery-scale investigations confirm that adjustment of ZSM-5 content in catalyst formulations allows selective control of the gasoline-to-olefin yield ratio, supporting the transition from fuel-oriented to petrochemical-oriented FCC process configurations [14].

Acidity Characterization and the Role of Brønsted–Lewis Site Distribution

Acid-site properties remain among the most important determinants of catalytic selectivity in FCC systems. However, modern research demonstrates that selectivity depends not only on total acid-site concentration but also on acid strength distribution and accessibility

within hierarchical pore networks. Advanced characterization techniques such as pyridine adsorption Fourier-transform infrared spectroscopy (Py-FTIR) and ammonia temperature-programmed desorption (NH_3-TPD) have therefore become essential tools for investigating acidity–selectivity relationships in zeolite catalysts [15].

Py-FTIR analysis enables differentiation between Brønsted and Lewis acid sites and provides quantitative information about their relative concentrations within zeolite frameworks. Experimental studies using this method demonstrate that increased Brønsted acidity promotes carbocation formation and enhances β-scission reactions, whereas excessive Lewis acidity favors dehydrogenation pathways leading to aromatic formation and coke deposition [16].

Similarly, NH_3-TPD measurements provide information about acid-site strength distribution and thermal stability. Catalysts with moderate acid strength exhibit improved selectivity toward gasoline-range hydrocarbons and light olefins compared with catalysts containing excessive concentrations of strong acid sites, which promote hydrogen-transfer reactions and condensation pathways [17].

Recent operando spectroscopy studies further reveal that acid-site behavior changes dynamically during catalyst aging and regeneration cycles. These findings indicate that acidity distribution should be interpreted as a time-dependent parameter rather than a fixed structural characteristic, reinforcing the importance of integrating deactivation effects into selectivity modeling frameworks [18].

Hierarchical zeolites containing accessible external Brønsted acid sites also demonstrate improved catalytic performance during processing of heavy feedstocks because bulky hydrocarbon molecules can interact with active centers without encountering severe diffusion limitations. This observation confirms that accessibility of acid sites represents a critical parameter controlling catalytic efficiency in modern FCC catalyst systems [19].

Diffusion-Controlled Cracking Mechanisms and Intermediate Lifetime Regulation

Diffusion processes within catalyst pore networks play a decisive role in regulating hydrocarbon conversion pathways in FCC systems. While intrinsic acidity determines the rate of carbocation formation, molecular transport behavior controls the residence time of intermediates inside catalytic environments and therefore influences the probability of secondary reactions such as hydrogen transfer and aromatic condensation [20].

Experimental tracer-diffusion studies demonstrate that restricted molecular mobility within microporous zeolites increases the lifetime of intermediate carbocations and promotes bimolecular reactions leading to coke formation. In contrast, hierarchical pore structures reduce diffusion resistance and facilitate rapid removal of reaction products from active catalytic zones [21].

Advanced pulsed-field gradient nuclear magnetic resonance investigations confirm that diffusion coefficients of hydrocarbons inside hierarchical zeolite frameworks are significantly higher than those observed in purely microporous materials. This increase in molecular mobility contributes directly to improved olefin selectivity and reduced coke formation during catalytic cracking reactions [22].

Diffusion limitations also influence catalytic selectivity indirectly through their interaction with acid-site accessibility. When intermediate species remain trapped near strong Brønsted acid sites, hydrogen-transfer reactions become more probable, resulting in increased formation of paraffins and aromatics. Conversely, shortened diffusion pathways promote β-scission reactions and enhance olefin production [23].

Recent multiscale modeling studies further demonstrate that diffusion effects must be considered alongside acidity distribution in order to accurately predict catalytic performance in FCC systems. These findings support the interpretation that catalytic selectivity is governed by the combined interaction of chemical and transport-related parameters rather than by intrinsic catalyst composition alone [24].

Integrated Implications for Selectivity Engineering in FCC Catalysts

Taken together, recent advances in hierarchical pore engineering, ZSM-5 selectivity optimization, acidity characterization techniques, and diffusion-resolved kinetic analysis demonstrate that catalytic selectivity in FCC systems emerges from the coordinated interaction of multiple structural and chemical parameters operating simultaneously within catalyst frameworks. These developments confirm that modern catalyst engineering strategies increasingly rely on integrated structure–acidity–diffusion optimization approaches capable of regulating hydrocarbon conversion pathways at the molecular scale.

Despite these advances, existing studies typically investigate these parameters separately rather than within a unified analytical framework. This limitation highlights the importance of developing conceptual selectivity models capable of linking pore architecture, acid-site distribution, diffusion behavior, and catalyst aging processes within a single explanatory structure, as proposed in the present study.

EXPERIMENTAL

Development of a conceptual structure–acidity–diffusion–deactivation model

In conventional catalysis studies, the experimental section usually describes catalyst synthesis, physicochemical characterization, and catalytic performance tests. The objective of the present work, however, is fundamentally different. Rather than reporting new laboratory experiments, this study develops an integrated conceptual framework that integrates the principal physicochemical factors governing catalytic selectivity in Fluid Catalytic Cracking (FCC) systems.

Accordingly, the "experimental" component of this work consists of the systematic construction of a conceptual model based on comparative analysis, theoretical synthesis, and critical integration of published experimental evidence. The proposed model is derived from experimentally established relationships reported in the literature concerning catalyst structure, acidity, diffusion behavior, deactivation mechanisms, and product selectivity. In this sense, the model itself represents the methodological core of the study and serves as the methodological framework through which published experimental evidence is systematically integrated into a unified explanatory model.

The conceptual model developed below therefore constitutes the experimental methodology of the present research and provides the basis for subsequent interpretation of catalyst selectivity mechanisms.

Unlike a traditional review article, the present study does not merely summarize previous findings but develops an original conceptual model that establishes new relationships among catalyst structure, acidity, diffusion, deactivation, and catalytic selectivity and proposes an original conceptual model that is intended to generate testable hypotheses for future experimental catalyst research. Therefore, the model-development procedure constitutes the principal methodological contribution of this work and fulfills the role of the experimental section required for conceptual catalyst studies.

Conceptual model of the structure–acidity–diffusion–deactivation–selectivity relationship

The structure–acidity–diffusion–deactivation framework proposed in this study interprets catalytic selectivity in Fluid Catalytic Cracking (FCC) systems as an emergent property resulting from the coordinated interaction of multiple catalyst parameters rather than from isolated physicochemical characteristics. Within this framework, selectivity is defined as a system-level response variable governed simultaneously by structural confinement effects, accessibility of active acid sites, transport-controlled residence time of intermediate species, and time-dependent catalyst evolution during industrial operation.

Unlike conventional catalyst-performance models that evaluate pore structure or acidity independently, the present framework integrates these variables into a unified analytical structure capable of explaining variations in hydrocarbon conversion pathways across different catalyst formulations and operating regimes.

Interaction Matrix of Selectivity-Determining Parameters

A key feature of the proposed conceptual framework is the recognition that selectivity is controlled not by individual catalyst parameters but by their mutual interactions. The relationship between the four principal parameter groups—structure (S), acidity (A), diffusion (D), and deactivation (Z)—may be represented as an interaction matrix describing their combined influence on catalytic behavior.

Within this matrix:

- structural parameters regulate transition-state stabilization through pore confinement effects,
- acidity characteristics determine carbocation formation probability,
- diffusion dynamics control intermediate lifetime inside catalytic environments,
- deactivation processes modify accessibility of active sites over time.

Importantly, these variables interact nonlinearly. For example, increased Brønsted acidity enhances cracking activity only when diffusion pathways remain sufficiently accessible. Similarly, hierarchical pore structures improve selectivity primarily when acid-site distribution is optimized for intermediate stabilization rather than condensation reactions. Thus, catalytic selectivity must be interpreted as the outcome of coupled structure–acidity–transport interactions rather than additive contributions of independent parameters .

Formal Interpretation of Selectivity Regimes

The proposed framework enables identification of distinct catalytic selectivity regimes corresponding to specific combinations of structural architecture and acidity distribution. These regimes provide a systematic basis for interpreting variations observed across industrial FCC catalyst formulations.

Gasoline-oriented selectivity regime

This regime is typically associated with catalysts dominated by large-pore zeolite frameworks and moderate hydrogen-transfer activity. Structural environments supporting stabilization of bulky carbocation intermediates promote formation of branched paraffins and aromatic gasoline components. Under such conditions, diffusion limitations remain moderate, allowing efficient conversion of vacuum gas oil fractions into high-octane gasoline products.

Olefin-oriented selectivity regime

This regime emerges in catalyst systems containing medium-pore zeolite structures capable of suppressing bimolecular hydrogen-transfer reactions. Reduced residence time of intermediate carbocations and enhanced β-scission pathways favor formation of propylene and butylene fractions. Such selectivity configurations are characteristic of refinery–petrochemical integration strategies designed to increase light olefin yield.

Aromatic and coke-oriented selectivity regime

This regime develops when excessive acidity strength combines with restricted diffusion pathways and progressive catalyst aging effects. Under these conditions, intermediate species undergo condensation reactions leading to formation of polyaromatic structures and coke precursors. Recognition of this regime is particularly important for predicting long-term catalyst stability and regeneration requirements.

Together, these regimes illustrate how catalytic selectivity shifts dynamically depending on structural accessibility, acidity distribution, and transport conditions within catalyst pore networks.

Industrial Applicability of the Conceptual Framework

Beyond its theoretical significance, the proposed structure–acidity–diffusion–deactivation framework provides practical guidance for modern FCC catalyst design strategies. In industrial environments, catalyst optimization requires balancing multiple performance objectives, including gasoline yield, light olefin production, coke suppression, and resistance to contaminant metals.

The framework supports these objectives by enabling systematic interpretation of how structural modifications influence hydrocarbon conversion pathways. For example, introduction of hierarchical pore connectivity improves accessibility of internal acid sites and enhances processing efficiency for heavy feedstocks. Similarly, controlled adjustment of acidity distribution allows selective suppression of hydrogen-transfer reactions and supports increased olefin production.

Another important practical implication of the model concerns catalyst aging behavior. Because industrial FCC catalysts operate under continuous reaction–regeneration cycles, selectivity evolves over time as pore accessibility and acid-site strength change. Incorporating the temporal parameter Z into selectivity interpretation therefore provides a more realistic basis for predicting long-term catalyst performance compared with static structural models ⏱.

Finally, the framework provides a conceptual foundation for integration with emerging data-driven catalyst optimization approaches. By representing selectivity as a multi-parameter function,

$$M = f(S, A, D, Z)$$

the model enables future development of predictive tools linking catalyst architecture with product distribution behavior. Such approaches may support next-generation FCC catalyst engineering strategies combining hierarchical pore design, optimized acidity control, and adaptive regeneration management.

RESULTS AND DISCUSSION

Integrated Interpretation of Catalytic Selectivity Formation

The structure–acidity–diffusion–deactivation framework proposed in this study enables a systematic interpretation of catalytic selectivity formation in Fluid Catalytic Cracking (FCC) catalysts by integrating structural confinement effects with transport dynamics and acidity distribution. Recent experimental and modeling studies confirm that catalytic selectivity cannot be explained solely by acid-site density or pore size independently, but instead emerges from the coordinated interaction between these parameters within hierarchical catalyst architectures [25–27].

Hierarchical zeolite catalysts provide particularly strong evidence supporting this interpretation. Electron microscopy and adsorption studies demonstrate that introduction of secondary mesoporous transport channels significantly improves accessibility of internal Brønsted acid sites and reduces residence time of intermediate carbocations within catalytic environments, resulting in enhanced olefin selectivity and reduced coke formation [28–29]. These findings confirm that transport accessibility represents a primary determinant of selectivity stability during heavy hydrocarbon conversion.

Similarly, comparative investigations of conventional and hierarchical ZSM-5 catalysts show that shortened diffusion pathways increase propylene selectivity through suppression of secondary hydrogen-transfer reactions responsible for olefin saturation [30]. This observation supports the interpretation that catalytic selectivity is governed not only by intrinsic acidity but also by spatial accessibility of active centers.

Structural Control of Selectivity Regimes

The proposed framework allows identification of distinct selectivity regimes

corresponding to specific catalyst architectures widely observed in industrial FCC systems.

Large-pore zeolites such as USY provide reaction environments capable of stabilizing bulky carbocation intermediates and promoting bimolecular hydrogen-transfer reactions responsible for gasoline-range hydrocarbon formation. Industrial catalyst-performance studies confirm that catalysts dominated by USY frameworks exhibit higher gasoline yield and improved aromatic selectivity compared with medium-pore zeolite systems [31–32].

In contrast, incorporation of ZSM-5 additives produces a shift toward olefin-oriented selectivity regimes by suppressing hydrogen-transfer reactions and enhancing β-scission pathways. Refinery-scale investigations demonstrate that optimized ZSM-5 loading increases propylene yield without significantly reducing total conversion efficiency, supporting refinery–petrochemical integration strategies [33–34].

Hierarchical zeolite catalysts represent an intermediate structural regime combining advantages of both microporous confinement and improved transport accessibility. Studies using nitrogen adsorption and pulsed-field gradient NMR techniques confirm that hierarchical pore connectivity enhances diffusion coefficients of hydrocarbon intermediates, thereby improving selectivity stability during processing of heavy feedstocks [35–36].

Together, these observations demonstrate that catalytic selectivity regimes can be interpreted as structural responses to pore architecture rather than as purely chemical effects determined by acidity strength alone.

Acidity–Diffusion Coupling Effects

Although acidity remains a primary determinant of catalytic cracking activity, recent research demonstrates that acid-site accessibility plays an equally important role in regulating hydrocarbon conversion pathways. Py-FTIR characterization studies confirm that catalysts containing balanced Brønsted and Lewis acid-site distributions exhibit improved selectivity stability compared with catalysts dominated by strong Lewis acidity promoting aromatization and coke formation [37–38].

NH_3-TPD investigations further indicate that moderate acid strength distributions favor selective β-scission reactions, whereas excessive concentrations of strong acid sites increase hydrogen-transfer probability and promote formation of paraffins and aromatics [39]. These findings support the interpretation that optimal selectivity requires controlled acidity rather than maximum acidity strength.

Importantly, accessibility of acid sites determines their effective catalytic contribution. Hierarchical zeolite systems containing externally accessible Brønsted acid centers exhibit higher cracking efficiency during processing of bulky hydrocarbons than conventional microporous catalysts with comparable total acidity values [40]. This observation confirms that acidity–diffusion coupling represents a key mechanism underlying selectivity regulation in modern FCC catalyst systems.

Diffusion-controlled residence time of intermediate carbocations further modifies reaction pathways. When intermediates remain trapped within confined microporous environments, secondary condensation reactions become more probable. Conversely, improved transport accessibility promotes rapid removal of intermediates and enhances olefin selectivity [41–42].

Time-Dependent Evolution of Selectivity During Catalyst Aging

An important contribution of the proposed conceptual framework is its ability to explain time-dependent variations in catalytic selectivity observed during industrial FCC operation. Catalyst properties evolve continuously during reaction–regeneration cycles due to coke deposition, hydrothermal dealumination, and accumulation of contaminant metals such as nickel and vanadium [43].

Operando spectroscopic investigations show that moderate coke deposition initially suppresses strong hydrogen-transfer reactions by blocking the most active Brønsted acid sites, temporarily increasing olefin selectivity. However, progressive coke accumulation

eventually reduces accessibility of active centers and decreases overall catalytic efficiency.

Nickel contamination further modifies selectivity behavior by promoting dehydrogenation reactions that increase hydrogen formation and accelerate condensation of unsaturated intermediates into coke precursors. Experimental catalyst-aging studies demonstrate that even small increases in nickel concentration significantly alter hydrogen balance in FCC reactions and shift product distribution toward lighter gaseous fractions

Vanadium contamination produces even more severe structural effects through destruction of framework aluminum atoms during regeneration cycles. Transmission electron microscopy investigations confirm that this process leads to irreversible loss of Brønsted acidity and deterioration of microporous structure, resulting in long-term selectivity instability.

These observations confirm that catalytic selectivity must be interpreted as a dynamic parameter evolving over time rather than as a static characteristic defined solely by initial catalyst composition.

Implications for Catalyst Design Strategies

The integrated interpretation developed in this study provides several important implications for modern FCC catalyst engineering. First, it demonstrates that optimization of hydrocarbon conversion pathways requires simultaneous control of pore architecture and acidity distribution rather than independent adjustment of individual catalyst parameters.

Second, hierarchical pore engineering improves accessibility of internal acid sites and enhances processing efficiency for heavy feedstocks containing large polycyclic hydrocarbons. Experimental catalyst-performance comparisons confirm that hierarchical zeolite catalysts exhibit reduced coke formation and improved regeneration stability compared with conventional microporous materials.

Third, incorporation of ZSM-5 additives enables selective enhancement of propylene production by suppressing hydrogen-transfer reactions and promoting secondary cracking of gasoline-range hydrocarbons. Industrial FCC optimization studies confirm that such catalyst formulations support increased olefin yield without significant loss of gasoline selectivity.

Finally, inclusion of time-dependent deactivation effects within the analytical framework provides a realistic basis for predicting long-term catalyst performance under industrial operating conditions. This capability represents an important advantage compared with conventional static catalyst-performance models.

Predictive Potential of the Proposed Framework

Within the structure–acidity–diffusion–deactivation framework proposed above, catalytic selectivity emerges from the coupled interaction of structural confinement effects, acid-site accessibility, molecular transport behavior, and catalyst aging processes rather than from any single dominant parameter.

Recent developments in multiscale simulation and machine-learning-assisted catalyst optimization suggest that such integrated parameter models may support predictive catalyst-design strategies capable of linking pore architecture and acidity distribution with product selectivity behavior in next-generation FCC systems.

Taken together, these results confirm that catalytic selectivity in FCC catalysts emerges from coordinated interactions between structural confinement, acid-site accessibility, diffusion dynamics, and catalyst aging processes. This interpretation provides a theoretical foundation for integrated catalyst-engineering strategies supporting both gasoline-oriented and olefin-oriented refinery configurations.

CONCLUSION

This study develops an integrated conceptual framework for interpreting catalytic selectivity formation in Fluid Catalytic Cracking (FCC) systems based on the coordinated interaction of catalyst structure, acidity characteristics, diffusion dynamics, and time-

dependent deactivation processes. Unlike conventional interpretations that evaluate these parameters independently, the proposed structure–acidity–diffusion–deactivation framework demonstrates that selectivity emerges as a system-level response governed by coupled physicochemical interactions within hierarchical catalytic environments.

The analysis shows that structural confinement effects within zeolite frameworks regulate transition-state stabilization and intermediate carbocation evolution, while accessibility and distribution of Brønsted acid sites determine the dominant cracking pathways responsible for gasoline and light olefin formation. At the same time, diffusion-controlled residence time of intermediates plays a decisive role in suppressing or promoting hydrogen-transfer reactions that influence aromatic formation and coke deposition. These findings confirm that catalytic selectivity cannot be interpreted as a function of acidity strength alone but must be understood as the result of integrated structure–transport–reactivity interactions operating simultaneously within catalyst pore networks.

An important contribution of the proposed framework is the incorporation of catalyst aging processes into selectivity interpretation. Coke deposition, hydrothermal dealumination, and accumulation of contaminant metals such as nickel and vanadium progressively modify pore accessibility and acid-site distribution during industrial operation, leading to dynamic shifts in product distribution behavior. Recognizing selectivity as a time-dependent parameter provides a more realistic representation of catalyst performance compared with static structural models traditionally used in FCC catalyst evaluation.

The framework also explains the functional differentiation observed in modern FCC catalyst architectures. Large-pore USY zeolites support gasoline-oriented selectivity regimes through stabilization of bulky intermediates and hydrogen-transfer reactions, whereas medium-pore ZSM-5 structures enhance light olefin formation by promoting β-scission pathways and suppressing secondary saturation reactions. Hierarchical micro–mesoporous catalysts combine these advantages by improving accessibility of active sites and reducing diffusion limitations associated with heavy hydrocarbon feedstocks. This integrated interpretation supports current trends in refinery–petrochemical process integration and advanced catalyst-design strategies.

From a methodological perspective, the proposed framework provides a systematic basis for linking catalyst architecture with product distribution behavior across different FCC operating regimes. By interpreting selectivity as an emergent property of interacting structural, chemical, transport, and temporal variables, the study contributes to the development of rational catalyst-engineering approaches capable of supporting both gasoline-oriented and olefin-oriented conversion strategies.

Future research should focus on experimental validation of the proposed framework through operando acidity characterization, diffusion-resolved kinetic measurements, and multiscale modeling of hierarchical pore networks. In addition, integration of data-driven catalyst optimization techniques and machine-learning-assisted selectivity prediction represents a promising pathway for transforming the present conceptual framework into predictive catalyst-design tools applicable to next-generation FCC systems.

Overall, the structure–acidity–diffusion–deactivation framework proposed in this study provides a coherent conceptual basis for understanding catalytic selectivity formation in FCC processes and supports the transition from empirical catalyst optimization toward integrated selectivity-oriented catalyst design methodologies.

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