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REVIEW: RADIATION-INDUCED RING-OPENING OF POLYCYCLIC TO MONOCYCLIC AROMATICS IN PRESENCE OF NANOSTRUCTURED CATALYST

M.K. Ismayilova, I.I. Mustafayev, T.A. Mahmudova, F.A. Salmanova,
K.V. Azizova, V.M. Safarova, I.E. Velizade, V.N. Poladova

Institute of Physics, Ministry of Science and Education of the Republic of Azerbaijan, Baku, Azerbaijan
ismayilovamehpara@gmail.com

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Abstract: The study focuses on heterogeneous catalysis for radiation-induced conversion of hydrocarbons into valuable products. It explains key mechanisms (cracking, dehydration, isomerization, hydrogenation, cyclization, and decyclization) and the role of different active sites. Advanced analytical methods are used to assess performance. Applications include petroleum refining, biofuels, plastic waste conversion, and renewable fuels, with improved results achieved using bifunctional catalysts like radiation-induced modified nanostructured bentonite clay.

Keywords: radiation-induced, irradiation, nanostructured bentonite clay, crude oil, heterogeneous catalysis.

1. Introduction

As the world shifts toward sustainable alternatives to petroleum, heterogeneous catalysis plays a vital role in converting biomass into hydrocarbon fuels, particularly biodiesel. Solid catalysts are increasingly replacing traditional homogeneous ones due to easier product separation and their ability to handle high free fatty acid (FFA) and moist feedstocks [1–4]. Methanol is most commonly used, though ethanol is also viable. Both acidic and basic solid catalysts—including metal oxides (CaO, MgO), calcined hydrotalcites, sulfonated resins, sulfated oxides, and bifunctional mixed oxides—have been extensively studied. Basic catalysts like CaO and hydrotalcites show high activity, especially under supercritical or microwave-assisted conditions, while solid acid catalysts excel in FFA esterification, enabling the use of waste oils. Bifunctional catalysts (e.g., Ti-Zn-Al oxides, vanadyl phosphates, and Fe–Zn double metal cyanides) combine acid-base properties and hydrophobicity, offering good stability, recyclability, and performance with low-quality feedstocks [5–17].

Researchers developed MeO-SBA-15 catalysts (ZnO, La_2O_3, CeO_2, NiO, and MgO) via a one-pot method for converting waste cooking oil (WCO) into liquid biofuels through catalytic thermal cracking at 460 °C. The mesoporous structure was preserved after metal incorporation [7, 11, 16]. ZnO-SBA-15 gave the highest liquid hydrocarbon yield (37.3%), while MgO-SBA-15 showed the lowest coke formation (2.1%) and produced biofuel with low acidity (46.2 mg KOH/g). The process significantly increased C_7–C_{15} hydrocarbons, yielding biofuels with properties close to conventional diesel [8–12, 17].

The petrochemical industry heavily relies on heterogeneous catalysis to transform hydrocarbon feedstocks into essential chemicals such as plastics, fertilizers, and solvents. Heterogeneous catalysts facilitate these processes by lowering activation energy and enhancing reaction rates, making them indispensable in large-scale chemical manufacturing. The following sections outline the key aspects of catalysis in petrochemical processes [11–15].

The processes covered in this study include cracking, hydrocracking, ring opening, cyclization, alkylation, oligomerization, etherification, and esterification, all of which play a significant role in refining operations and the production of synthetic chemicals (Table 1).

Table 1

Reaction types and catalyst examples.

Reaction type	Catalyst
Cracking	Zeolite; SiO_2–Al_2O_3
Hydrocracking	Ni–Mo; Zeolite
Ring-opening	Acid catalysts (e.g., H_2SO_4; Pt, Ru, Rh, Ir-supported; Nanostructured bentonite clay)
Cyclization	Zeolite; phosphoric acid
Alkylation	HF; H_2SO_4
Oligomerization	Zeolite; solid acid catalysts
Etherification	Acidic ion-exchange resins
Esterification	H_2SO_4; solid acid catalysts

Cracking involves the thermal or radiation-catalytic decomposition of long-chain hydrocarbons into shorter, more valuable fractions. Hydrocracking integrates catalytic cracking with hydrogenation to reduce aromatic content and improve fuel quality [12, 14, 18]. Ring-opening reactions target cyclic hydrocarbons, using acidic or metallic catalysts to convert them into linear or branched structures. Cyclization facilitates the formation of ring compounds, including aromatics, often through acid catalysis or thermal methods. Alkylation combines light olefins with isobutane to produce high-octane gasoline components, while oligomerization transforms smaller olefins into longer-chain hydrocarbons for fuels and lubricants. Etherification and esterification are widely used for producing fuel additives and biodiesel, respectively [1, 2].

Other key transformations include hydrogenation and dehydrogenation, which convert olefins to paraffins or facilitate aromatization processes. Isomerization is commonly used to improve fuel properties, such as increasing gasoline octane or enhancing the cold-flow performance of diesel, kerosene, and waxes. The complexity of product analysis depends greatly on the feedstock [5, 7, 8, 11]. Model compounds, such as pure n-decane, produce predictable and simpler product distributions, making them easier to analyze. In contrast, complex feedstocks like biomass-derived oils generate a broad spectrum of products, requiring advanced analytical techniques for accurate characterization [6, 13, 14].

Polyaromatic hydrocarbons, polycyclic aromatics, or polyarenes are a major product fraction of multiple classical, waste, and bio-refinery operations [6, 11–17]. They have an extremely negative environmental impact, a minimal market, and a lowering demand. Parallelly, low-alkylated single-ring arenes or monoaromatics (benzene, toluene, and xylenes, the so-called BTX fraction) are highly demanded due to their applications as chemicals or fuels. Herein, we review the status of applied polyaromatic selective ring-opening by hydrocracking into monoaromatics. This review addresses the involved mechanisms, applicable catalysts [5–9, 12, 14, 16, 19],

Polyaromatics are non-polar species having only carbon and hydrogen. Their chemical structure comprises two or more fused aromatic rings bonded in different arrangements with a pair of carbon atoms shared among their rings [4, 7, 9, 10]. Several hundred polyaromatics have been identified; Fig. 1 shows the molecular structures of some of the most abundant polyaromatics.

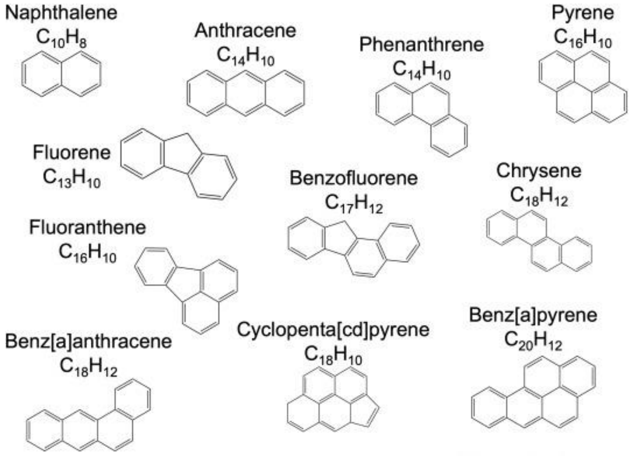

Fig. 1. Structures of some of the most common polyaromatics.

Aromatic-rich streams are generally formed as heavy (often residual) byproducts in the most important refinery units: distillation, fluid catalytic cracking (FCC), delayed coking, and breaking or steam cracking units [4, 5, 8–13]. These highly aromatic streams have a relatively low commercial value, but their composition imparts potential for upgrading to lighter chemicals, including (alkylated) monoaromatics such as benzene, toluene, and xylenes (BTX) [1, 19]. Recently, considerable progress has been made in developing catalytic strategies to convert heavily aromatic feedstock, either produced as refinery byproducts [12, 13, 17, 18].

The mechanistic aspects of C–C bond cleavage reactions of cyclopropane compounds within selective ring opening conversion have been covered in detail by Vicente [12]. Hydrogenation and hydrogenolysis reactions occur on the metallic sites of the catalyst, whereas isomerization and cracking reactions are carbocation-mediated and occur on the acidic sites [13]. A broad classification is needed, but a certain degree of C–C hydrogenolysis on the metallic sites [14, 15] and other reactions, such as coking, also occur. Hydrogenation involves alkene-olefin hydrogenation, one of the fastest reactions in hydroprocessing, and aromatics hydrogenation in a later stage, as the energy barrier to break the aromatic resonance is greater than for the olefins [6, 10]. The latter step is sometimes called hydrodearomatization (HDA) when targeting the removal of polyaromatics [16]. Although most studies focus primarily on diaromatic compounds, triaromatic compounds are essential representatives of anthracene and phenanthrene in industrial streams. An example of the case of naphthalene is provided in Fig. 2 (a, b).

Catalytic hydrogenation is the most effective route for converting low-grade and complex HCs into useful chemicals [1, 2, 8, 11, 16, 18]. The partial hydrogenation of naphthalene to tetralin is the main step in this reaction, so it requires bifunctional catalysts containing both active metals and acid sites that can operate at high hydrogen pressure and reaction temperature. Most discrete kinetic modeling approaches have been performed using either decalin or tetralin as the feedstock for SRO [10–14, 17, 19]. An example of the case of decalin is provided in Fig. 3a [9, 10, 17, 19]. These models group the chemical compounds based on their physicochemical similarities, such as chemical nature Fig. 3b or boiling point range Fig. 3c; the latter is generally the predominant criterion. The C_{10} ring-opening products are lumped in such a way that the individual ring-opening activity of a specific catalyst can be assessed in an isolated manner [1, 2, 8]. Additional saturated cyclic compounds with fewer than ten carbon atoms are considered cracking products [1, 15, 17, 19]. Through the sensible lumping of individual species, capturing shifting behaviors like the hydrogenation/dehydrogenation reactions with temperatures can be attained. One of the main objectives of SRO is to maintain the number of carbon atoms in each molecule [12, 16]. The potential of discrete lumping for evaluating SRO routes alone relies on a suitable identification and quantification of the reaction products. Hence, this methodology is limited when operating with heavy polyaromatic feedstocks due to the intrinsic analytical limitations for obtaining a comprehensive description of the composition of the reaction medium [1, 2, 13, 16–19].

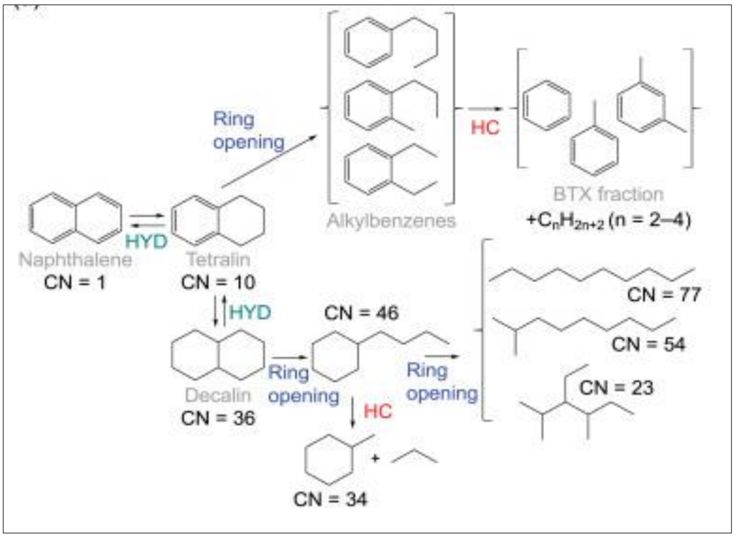

Fig. 2. (a) Proposed mechanism for the ring-opening of naphthalene as a model compound and (b) schematic representation of the bifunctional reaction mechanism for the hydrocracking of paraffins

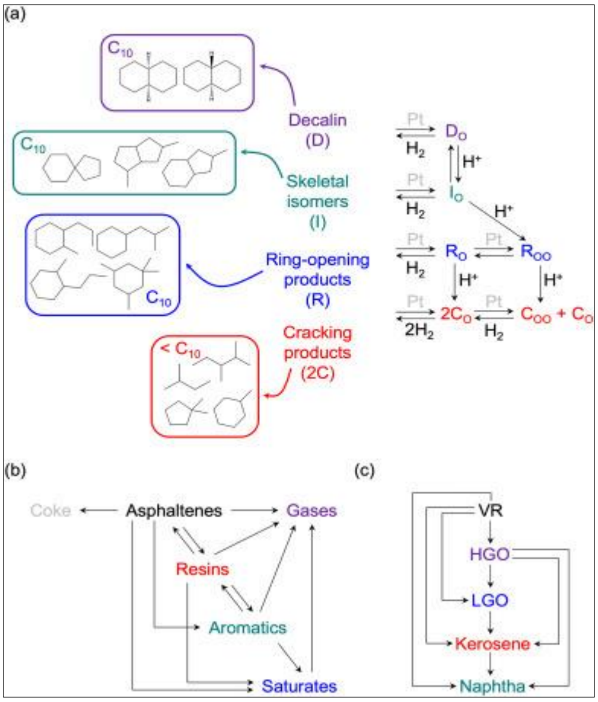

Fig. 3. Schematic diagram showing (a) a lump-based discrete kinetic model for the SRO of decalin over a Pt-modified β zeolite (denote an olefin and diene, respectively) and lump-based continuous models for the hydroprocessing of (b) a heavy oil and (c) a vacuum residue (VR, vacuum residue; HGO, heavy gas oil; LGO, light gas oil)

Due to the complexities associated with realistic feedstock processing, there is a gap in the literature describing the transformation of real feedstocks derived from crude oil or waste, which would allow for results with greater industrial applicability, despite the limited information due (mainly) to analytical limitations [1, 2, 8, 9, 20, 21].

One of the main tasks of SRO is to find a suitable catalyst [1, 2, 8, 11, 20–22]. Fig. 4 shows the scheme of the radiation-induced ring-opening reaction in the presence of nanostructured bentonite clay under vacuum conditions at room temperature.

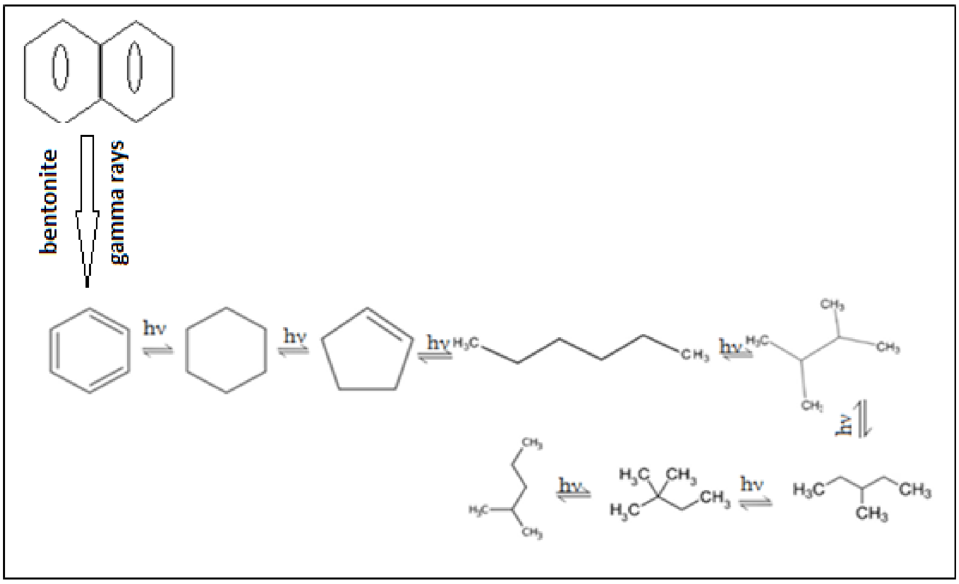

Fig. 4. Schematic representation of the radiation-induced ring opening of polycyclic to monocyclic aromatics and aliphatic products in the presence of nanostructured catalyst – sodium bentonite clay

2. Conclusions

- In selective ring opening reactions, catalyst design (the selection of the active metallic phase and support properties) must meet the requirements to provide the complex reaction network balance that is required for BTX: benzene, toluene, and xylenes production.
- The upgrading of residual polyaromatics to BTX is an interesting alternative. In fact, despite the existence of technologies that convert low-quality naphtha into BTX, fuel market predictions still justify heavy oil upgrading. Furthermore, a tight integration of refinery and petrochemical complexes is essential, wherein the gross margin per barrel of crude oil could be increased to $30, especially in the short- and mid-term, while other avant-garde alternatives around the conversion of crude to chemicals still remain impractical.
- Among the technologies studied, radiation-induced ring-opening reactions are environmentally friendly.
- Irradiated nanostructured bentonite clay can be used as modified mesoporous materials for selective ring-opening reactions.

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ОБЗОР: РАДИАЦИОННО-ИНДУЦИРОВАННОЕ РАСКРЫТИЕ КОЛЬЦА ПОЛИЦИКЛИЧЕСКИХ АРОМАТИЧЕСКИХ СОЕДИНЕНИЙ ДО МОНОЦИКЛИЧЕСКИХ АРОМАТИЧЕСКИХ СОЕДИНЕНИЙ В ПРИСУТСТВИИ НАНОСТРУКТУРИРОВАННОГО КАТАЛИЗАТОРА

М.К. Исмаилова, И.И. Мустафаев, Т.А. Махмудова, Ф.А. Салманова, К.В. Азизова, В.М. Сафарова, И.Э. Вализаде, В.Н. Поладова

Резюме: Настоящее исследование, посвящено гетерогенному катализу радиационно-индуцированного превращения углеводородов в ценные продукты. В нем объясняются ключевые механизмы (крекинг, дегидратация, изомеризация, гидрирование, циклизация, дециклизация) и роль различных активных центров. Для оценки эффективности используются передовые аналитические методы. Области применения включают нефтепереработку, биотопливо, переработку пластиковых отходов и возобновляемые виды топлива, при этом улучшенные результаты достигаются с использованием бифункциональных катализаторов, таких как радиационно-индуцированная модифицированная наноструктурированная бентонитовая глина.

Ключевые слова: радиационно-индуцированное превращение, облучение, наноструктурированная бентонитовая глина, сырая нефть, гетерогенный катализ.

XÜLASƏ: RADİASİYA NƏTİCƏSİNDƏ NANOSTRUKTURLU KATALİZATORUN İŞTİRAKI İLƏ POLİTSİKLİK BİRLƏŞMƏLƏRDƏN MONOTSİKLİK AROMATİK KARBOHİDROGENLƏRƏ KİMİ HALQANIN AÇILMASI

M.K. İsmayılova, İ.İ. Mustafayev, T.Ə. Mahmudova, F.A. Salmanova, K.V. Əzizova, V.M. Səfərova, İ.E. Vəlizadə, V.N. Poladova

Xülasə: Tədqiqat işi politsiklik karbohidrogenlərin radiasiyanın təsiri nəticəsində qiymətli məhsullara çevrilməsinin heterogen katalizinə həsr edilmişdir. Məqalədə əsas mexanizmlər (krekinq, dehidrasiya, izomerləşmə, hidrogenləşmə, siklləşmə, detsiklizasiya) və müxtəlif aktiv mərkəzlərin rolu izah edilir. Eksperimentlərin effektivliyini qiymətləndirmək üçün qabaqcıl analitik üsullardan istifadə edilmişdir.

Tətbiq sahələrinə neft emalı, bioyanacaq, plastik tullantıların emalı və bərpa olunan yanacaq növləri daxildir, bununla yanaşı təkmilləşmiş nəticələrin radiasiyanın təsiri altında nanostrukturlu bentonit gili kimi ikifunksiyalı katalizatorlardan istifadə etməklə əldə edildiyi göstərilmişdir.

Açar sözlər: radiasiya nəticəsində yaranan, şüalanma, nanostrukturlu bentonit gili, xam neft, heterogen kataliz.