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Selective Hydrogenation of Benzene in the Presence of Aromatic Hydrocarbons: Mechanisms, Catalysts, and Modern Approaches

Aiken Manassova[1], Seitkhan Azat[2*], Rachid Amrousse[3], Kainaubek Toshtay[1]**

[1]Al-Farabi Kazakh National University, Al-Farabi Ave. 71, 050040, Almaty, Kazakhstan
[2]Satbayev University, Satbayev Str. 22, Almaty, 050000, Kazakhstan
[3]Chouaïb Doukkali University, Faculty of Sciences, 24000 El Jadida, Morocco

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Abstract

This review article systematizes current knowledge on the catalytic hydrogenation of benzene as a key process in petrochemistry, environmental protection, and hydrogen energy technologies. The fundamental mechanisms of benzene ring activation and molecular hydrogen dissociation on transition metal surfaces are discussed, with particular emphasis on the disruption of aromatic stability as the rate-limiting step of the reaction. Special attention is given to the challenge of achieving selective benzene hydrogenation in the presence of other aromatic compounds, a situation typical of reformate and pyrolysis gasoline fractions. The influence of the active metal type (Ni, Pd, Pt, Ru), catalyst supports (oxide, zeolitic, carbon-based, and natural materials), and reaction parameters (phase, temperature, and hydrogen pressure) on catalytic activity, selectivity, and stability is systematically analyzed. Competitive adsorption among aromatic compounds, the role of electronic and steric effects of substituents, and mass-transfer limitations in liquid-phase systems are also examined. Results obtained for both industrial and emerging catalytic systems are summarized, including catalysts for the deep and partial hydrogenation of benzene, as well as their potential applications in liquid organic hydrogen carrier (LOHC) technologies. Achieving high selectivity therefore requires comprehensive optimization of catalyst composition, support structure, and process conditions, which defines the main directions for future research.

1. Introduction

Hydrogenation of benzene is one of the fundamental reactions in catalytic chemistry. This process is of both practical and theoretical importance, as it represents a model system for understanding the mechanisms of aromatic ring activation, the loss of aromatic stability, and the dissociation and activation of molecular hydrogen on catalytic surfaces. From an industrial perspective, benzene hydrogenation plays a crucial role in fuel refining technologies. In particular, the benzene content in gasoline fractions obtained from catalytic reforming and pyrolysis processes is strictly regulated by international environmental standards due to the well-established carcinogenic nature of benzene. Consequently, the development of efficient catalytic systems for the selective hydrogenation of benzene has become an important task for both petroleum refining and environmental protection.

The benzene content in automotive gasoline is directly related to the characteristics of petroleum refining processes. The primary source of benzene is catalytic reforming, a process involving the aromatization of low-octane hydrocarbons to increase their octane number [1]. In the product stream of

*Corresponding authors.
E-mail address: seytkhan.azat@gmail.com;
kainaubek.toshtay@kaznu.kz

this process, the fraction of aromatic compounds can reach up to 70%, while the benzene content in some cases may amount to 10–14% [2]. Additional sources of benzene include pyrolysis gasoline (a by-product of ethylene production), as well as products of catalytic and thermal cracking. As a result, in the absence of additional fuel purification steps, the benzene concentration may significantly exceed current environmental regulations (e.g., ≤1 vol.% in Europe and the United States) [3–5].

Incomplete combustion of benzene and other aromatic hydrocarbons leads to the formation of polycyclic aromatic hydrocarbons (PAHs). One of the most hazardous representatives of this group is benzo[a]pyrene, which, according to the classification of the International Agency for Research on Cancer (IARC), belongs to Group 1 carcinogens. Pyrogenic PAHs are formed during the high-temperature incomplete combustion of organic substances and are widely distributed persistent environmental pollutants. These compounds can accumulate in soil and plants and, even at extremely low concentrations, exhibit mutagenic and carcinogenic effects. Therefore, the formation of such hazardous products during the incomplete combustion of benzene and its derivatives significantly increases the importance of catalytic benzene removal from fuel compositions in order to protect the environment and human health [6–8].

Alongside its importance for environmental safety, benzene hydrogenation also has strategic significance from the perspective of energy technologies and sustainable development. In recent years, this reaction has been considered one of the promising approaches for hydrogen storage and transportation. The high hydrogen storage capacity of the benzene ring, together with the possibility of reversible hydrogen release from saturated hydrocarbons, allows benzene to be used as a chemical hydrogen carrier. This approach opens new opportunities for integrating hydrocarbon chemistry into future hydrogen energy systems [9, 10].

At the same time, the selective hydrogenation of benzene represents a highly complex scientific and technological challenge. The aromatic ring of benzene is stabilized by a strong π-electron system, and its hydrogenation therefore requires overcoming a relatively high activation energy. In addition, gasoline fractions typically contain significant amounts of unsaturated hydrocarbons, particularly alkenes, which are hydrogenated much more readily.

As a result, many industrial catalysts preferentially saturate the C=C bonds of alkenes, leading to a decrease in the fuel's octane number. Even specially designed catalytic systems often exhibit only moderate selectivity toward benzene hydrogenation [11–13].

Thus, achieving high selectivity toward benzene in complex multicomponent systems, where competing reactions occur and high-octane fuel components must simultaneously be preserved, remains one of the key scientific and industrial challenges in modern catalytic chemistry. In this context, the present review provides a systematic analysis of the current understanding of the mechanisms underlying benzene hydrogenation. The main types of metal-based catalysts used in both industrial and model systems are discussed, and data on the influence of active metal nature, support materials, and surface structural characteristics on catalytic activity, selectivity, and stability are comprehensively summarized. Special attention is given to the comparison of classical and modern catalytic systems, as well as to the discussion of future directions for the development of selective benzene hydrogenation processes in light of increasingly stringent environmental regulations and the transition toward more sustainable hydrocarbon processing technologies.

2. General theoretical principles of catalytic benzene hydrogenation

Catalytic hydrogenation is one of the fundamental processes in heterogeneous catalysis. In this reaction, molecular hydrogen (H_2) reacts with unsaturated compounds on the surface of transition metals, leading to the formation of new C–H bonds. Hydrogenation reactions are widely used in industrial and laboratory processes, including hydrocarbon purification, saturation of aromatic compounds, and the synthesis of various organic chemicals [14–16].

The hydrogenation reaction on the catalyst surface proceeds through two main interconnected stages. The first stage involves the activation of molecular hydrogen: the H_2 molecule adsorbs onto the metal surface and dissociatively splits into two hydrogen atoms (H*). In the next stage, the unsaturated substrate, such as benzene, adsorbs onto the catalyst surface through its π-electron system and enters a reactive state [17–19].

Metals such as Ni, Pd, Pt, Rh, and Ru are widely used as catalysts because both hydrogen molecules and the substrate can adsorb simultaneously on their surfaces and interact at the atomic level [20]. The main advantage of these metals is their high efficiency to activate molecular hydrogen. In the gas phase,

the H–H bond is very strong (436 kJ·mol^{-1}); however, on the surface of Ni, Pd, or Pt, it dissociates almost without an energy barrier, forming mobile hydrogen atoms [21]. These atoms rapidly migrate across the metal lattice and, if necessary, can transfer to the support surface, creating a reservoir of active hydrogen available for the reaction [22].

The interaction of benzene with the catalyst surface directly depends on the nature and structure of the metal surface. On smooth, closely packed surfaces, such as Pt(111), the benzene ring adopts a flat orientation, forming an η^6-π complex [23]. In this configuration, the π electrons of benzene overlap with the d orbitals of the metal, leading to stabilization of the adsorbed molecule [24, 25]. In contrast, on more open and reactive surfaces, such as Ni(100) or Ru(0001), adsorption is stronger. In these cases, the π-electron system of benzene is partially distorted, and aromaticity is reduced, which facilitates the subsequent addition of atomic hydrogen [26]. Therefore, the mode and geometry of benzene adsorption on the metal surface are critical factors that determine both the ease and the direction of its hydrogenation.

Benzene hydrogenation proceeds according to the classical Horiuti–Polanyi mechanism. This mechanism (Fig. 1) describes the stepwise, sequential addition of hydrogen atoms to the benzene ring. Hydrogen atoms adsorbed on the catalyst surface (H*) are successively added to the carbon atoms of the ring, leading to the gradual disruption of its aromaticity. Ultimately, this process results in the formation of the fully saturated product, cyclohexane, under appropriate reaction conditions [11, 15].

The first hydrogen addition is the most critical and energetically demanding stage of the reaction. At this step, one of the carbon atoms undergoes a transition from an sp^2-hybridized state to an sp^3-hybridized state, resulting in disruption of the π-electron delocalization in the aromatic ring. This leads to the formation of a metal-bound cyclohexadienyl intermediate (C_6H_7) [27, 28].

According to computational studies, this step requires overcoming the resonance energy of benzene, which is approximately 150 kJ·mol^{-1} [28]. However, the presence of a catalyst significantly reduces this energy barrier. Density functional theory (DFT) calculations indicate that the activation energy for the first hydrogen addition on Ni, Pd, and Pt surfaces generally ranges from 60 to 100 kJ·mol^{-1}, with Pt sometimes exhibiting slightly lower values [27, 29]. In most cases, this step is considered the rate-determining stage of the process. Once the first hydrogen atom is added, the ring structure becomes "softened," and subsequent hydrogen additions proceed much more readily.

Figure 2 shows the hydrogenation enthalpies of benzene, 1,3-cyclohexadiene, and cyclohexene to cyclohexane. For cyclohexene (−120 kJ·mol^{-1}) and 1,3-cyclohexadiene (−240 kJ·mol^{-1}), the enthalpies follow typical alkene/diene behavior, changing approximately proportionally to the number of double bonds. In contrast, for benzene, the experimentally observed hydrogenation enthalpy (−208 kJ·mol^{-1}) is significantly lower than the expected value (−360 kJ·mol^{-1}), reflecting the presence of aromatic stabilization energy of approximately 150 kJ·mol^{-1} [30].

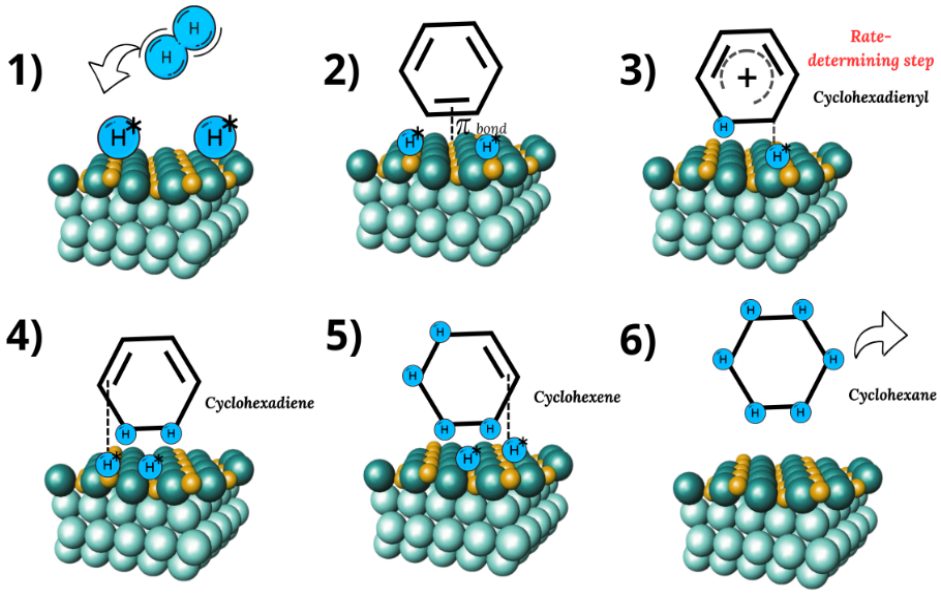

Fig. 1. Stepwise mechanism of benzene hydrogenation on the catalyst surface.

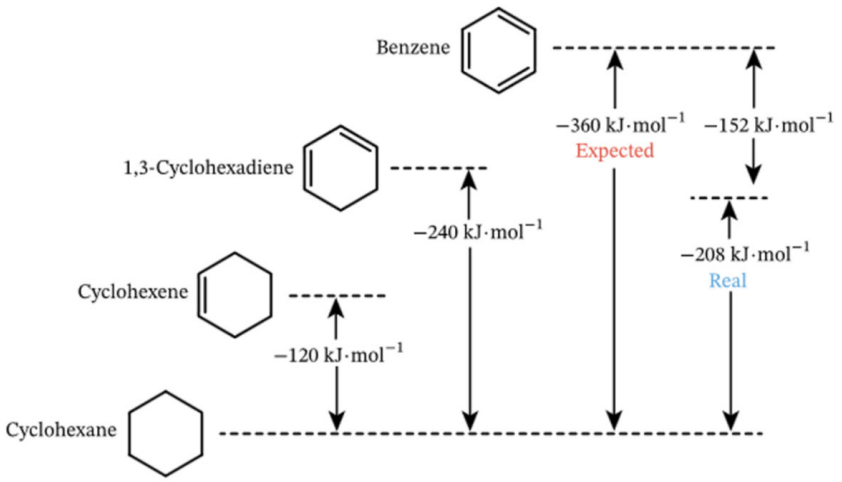

Fig. 2. Hydrogenation enthalpies of benzene and its derivatives [30].

After the initial disruption of the aromaticity of the benzene ring, its structure becomes "softened," and the subsequent hydrogenation of cyclohexadienyl and cyclohexene-like intermediates proceeds similarly to the hydrogenation of ordinary dienes and alkenes. Overall, the hydrogenation of benzene to cyclohexane is an exothermic process, with a total enthalpy change of approximately −200 kJ·mol^{-1}. However, the enthalpies of the individual steps and the corresponding energy barriers strongly depend on the nature of the interaction with the metal surface and can vary by several tens of kJ·mol^{-1} [31–33].

In the final stage of hydrogenation, the last C=C bond is saturated, yielding fully hydrogenated cyclohexane. According to density functional theory (DFT) calculations, the energy barrier for this step typically ranges from 60 to 100 kJ·mol^{-1}; however, under conditions of high hydrogen surface coverage, the effective barrier can be significantly reduced [32, 34]. Cyclohexane adsorbs on the metal surface much more weakly than benzene, which forms a π-complex; its interaction with the surface is governed primarily by van der Waals forces. On Pt-type surfaces, the adsorption energy of cyclohexane is approximately −50 to −60 kJ·mol^{-1}. This relatively weak interaction facilitates rapid product desorption, minimizes blockage of active sites, and enables prolonged continuous catalyst operation with high selectivity [35–37].

3. Importance of selective hydrogenation of benzene

The hydrogenation of benzene is one of the strategically important processes in modern petrochemistry and environmental technologies. This process plays a significant role not only from a chemical perspective but also in the fields of energy security and environmental protection.

First, reducing the benzene content in gasoline or its complete removal has become an important environmental and public health objective. Benzene is an aromatic hydrocarbon with a high octane number; however, it exhibits pronounced carcinogenic properties. The International Agency for Research on Cancer and the United States Environmental Protection Agency classify benzene as a Group 1 carcinogen. In this regard, modern environmental regulations, such as Euro 5 emission standard and Euro 6 emission standard and subsequent standards, limit the maximum allowable benzene content in motor fuels to no more than 1 vol.% [38–40]. One of the most effective approaches to meet these requirements is catalytic hydrogenation. During this process, the benzene molecule reacts with hydrogen, the aromatic ring becomes saturated, and it is converted into a chemically inert and non-toxic cycloalkane [5]. As a result, the environmental characteristics of the fuel are significantly improved, and the concentration of toxic components in engine exhaust emissions is reduced.

The selectivity of modern catalysts toward the complete conversion of benzene to cyclohexane is extremely high–under optimal conditions, the yield of cyclohexane can exceed 99%. For example, it has been experimentally demonstrated that efficient catalytic systems such as Pd/Al_2O_3 are capable of completely hydrogenating benzene at temperatures of around 200 °C [41].

The main products of benzene hydrogenation are cyclohexane and cyclohexene, both of which are valuable chemical feedstocks. Cyclohexane is primarily used as an intermediate: approximately 54%

of its global production is directed toward the manufacture of adipic acid for Nylon 6,6, about 39% is used for the synthesis of caprolactam for Nylon 6, and the remaining 7% is utilized in the production of solvents, insecticides, plasticizers, and other chemical products [42, 43]. The demand for nylon as an engineering thermoplastic for resins and film materials and consequently for cyclohexane is increasing at an average rate of approximately 6% per year. In addition, cyclohexane is widely employed in chemical synthesis as an inert solvent and as a precursor in the production of oxygen-containing organic compounds. Cyclohexene, in turn, is an important intermediate in the synthesis of a variety of organic compounds and polymers, exhibiting high reactivity in transformations leading to oxygenated products and functional monomers [44]. Thus, benzene hydrogenation represents a key process in the petrochemical industry, supporting the sustainable production of synthetic materials and polymer feedstocks (Fig. 3).

At present, a new research direction in the field of benzene hydrogenation is the investigation of its potential use in liquid organic hydrogen carrier (LOHC) systems for the storage and transportation of hydrogen energy. Within this concept, benzene and its hydrogenation products–cyclohexane or methylcyclohexane–are capable of "binding" hydrogen in the form of chemical bonds and subsequently releasing it during the dehydrogenation process (Fig. 4). Such reversible systems are considered an efficient and safe method for hydrogen storage and transport [45, 46].

As a result of the catalytic dehydrogenation of cyclohexane, the released hydrogen can be directly utilized in fuel cells, while the formed benzene can be hydrogenated again, ensuring the continuity of the cycle. This type of closed chemical loop makes it possible to store hydrogen in a liquid form with high energy density and improved safety, which in turn represents an important step in the development of the hydrogen energy economy.

Cyclic alkanes and aromatic compounds containing one or several six-membered rings are considered particularly promising reversible liquid organic hydrogen carrier (LOHC) systems, because they are chemically stable, remain in the liquid state under ambient conditions, and are capable of storing hydrogen with a mass fraction of about 6–7% at relatively high density [47]. The benzene–cyclohexane pair represents one of the simplest examples of such LOHC systems: during the dehydrogenation of one cyclohexane molecule, three molecules of H_2 are released (corresponding to a total hydrogen mass fraction of about 7.2 %), while benzene is formed [48]. An advantage of this system is that both benzene and cyclohexane are widely available chemical products and exist in the liquid state under normal conditions, with boiling points of approximately 80 °C [41].

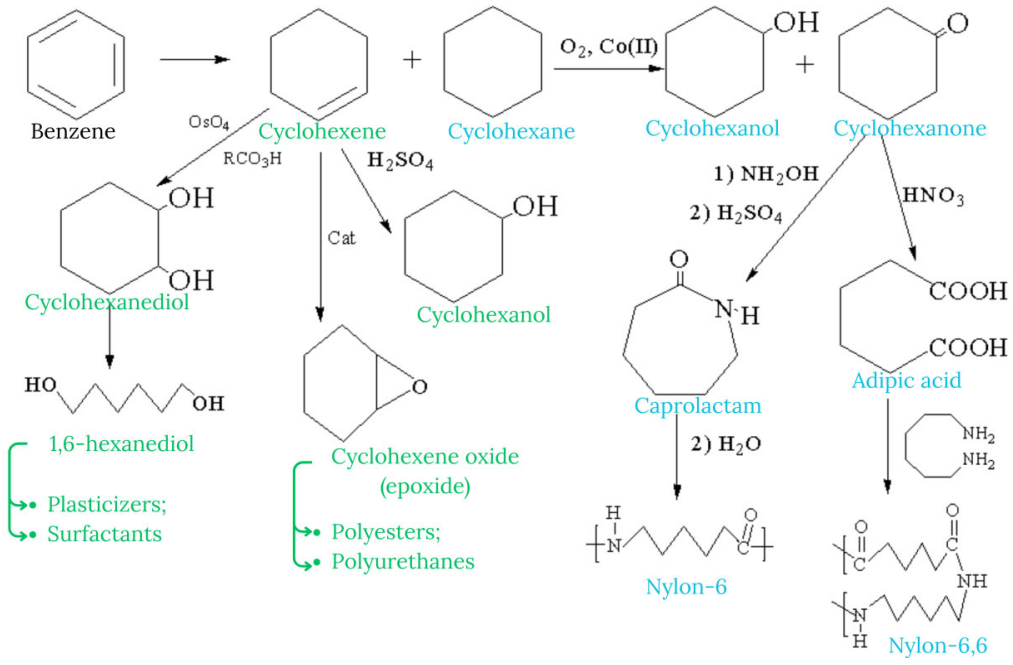

Fig. 3. Industrially important compounds derived from the products of benzene hydrogenation, cyclohexane and cyclohexene.

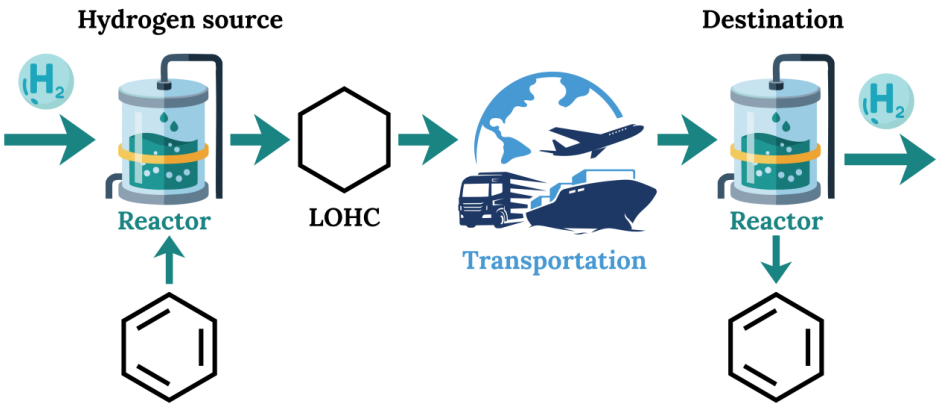

Fig. 4. Principle of a liquid organic hydrogen storage and transportation system.

Overall, the hydrogenation of benzene, while being one of the classical catalytic processes, represents a multifaceted system at the intersection of modern science and industry. This reaction is aimed at reducing environmental pollution, improving the quality of motor fuels, producing highly valuable chemical feedstocks, and contributing to the development of the future hydrogen economy. Such a comprehensive role determines its significance in chemical engineering, environmental technologies, and energy materials science.

4. The concept of selective hydrogenation and the influence of other aromatic compounds on selectivity

Selective hydrogenation is a process in which, in the presence of multiple aromatic compounds, only one is hydrogenated, while the other aromatic components remain unreacted and unchanged. This approach is particularly important in motor fuel production, where it is necessary to remove harmful aromatic compounds such as benzene while retaining other aromatics that enhance fuel performance. Restrictions on benzene content in gasoline have been introduced due to its pronounced carcinogenic properties. To meet these requirements, the selective hydrogenation strategy is widely applied during the processing of reformate and pyrolysis naphthas, targeting the hydrogenation of the benzene ring exclusively to cyclohexane or other naphthenes within an aromatic mixture. In this area, catalysts based on Pt, Pd, Ru, and Ni are actively studied [49, 50]. However, traditional hydrogenation catalysts often hydrogenate all aromatic rings simultaneously, which significantly complicates the achievement of the desired selectivity.

The decrease in selectivity in the presence of multiple aromatic compounds is generally attributed to two main factors: (i) competitive adsorption on the catalyst surface and (ii) differences in the intrinsic hydrogenation rates of the adsorbed molecules.

During competitive adsorption, different aromatic compounds compete for the same active metal sites. Spectroscopic and catalytic studies indicate that alkyl-substituted aromatics (toluene, xylenes, butylbenzene, etc.) adsorb more strongly on most Pd- and Pt-based catalysts than benzene, an effect that is particularly pronounced in systems where electron-deficient Pd clusters are formed [51, 52]. Moreover, alkylbenzenes can interact strongly with the acidic sites of the support, promoting a local concentration of these molecules near the metallic particles.

As a result, a significant portion of the surface active sites is occupied primarily by toluene, xylenes, and other alkylbenzenes, which displace the more weakly adsorbing benzene. Several recent studies on the hydrogenation of benzene–toluene mixtures over Pt-, Pd-, and Ru-containing catalysts have shown that at the initial stage, the conversion of alkylated aromatics is often higher than that of benzene, and that achieving selective hydrogenation of benzene to cyclohexane requires careful tuning of the catalyst composition and structure, including optimization of the metal, support, and acidic properties [52–55].

A second important factor limiting selectivity is the difference in the intrinsic hydrogenation rates of various aromatic compounds. After adsorption on the catalyst surface, the reaction rate is governed by the electronic structure of the π-system of the aromatic ring, as well as by the nature and steric characteristics of substituents ($–CH_3$, $–C_2H_5$, etc.). Alkyl groups, acting as electron donors, increase the electron density of the aromatic ring and can modify both the metal–adsorbate interaction and the transition-state energy. However, the overall effect strongly depends on the catalyst type: in some systems, it

enhances the reaction rate, whereas in others, steric hindrance leads to a decrease in reactivity. For example, in the vapor-phase hydrogenation of individual aromatic compounds over Pd catalysts supported on SiO_2-Al_2O_3 and TiO_2, the turnover frequencies decrease in the order: benzene > toluene ≳ p-xylene ≳ m-xylene > o-xylene, indicating that benzene hydrogenation can be intrinsically faster than that of methyl-substituted aromatics in these systems [51]. In contrast, several studies on the competitive hydrogenation of alkyl-substituted aromatics have shown that alkylbenzenes such as toluene and xylenes can exhibit higher hydrogenation activity than benzene due to the stronger adsorption and electron-donating effects of alkyl substituents [56]. Thus, the actual selectivity in aromatic mixtures is determined by a combination of adsorption strength and intrinsic hydrogenation kinetics. Within practical ranges of temperature and pressure, competitive adsorption often plays a decisive role, whereas as the system approaches equilibrium, thermodynamic factors increasingly contribute [57].

4.1. Influence of the adsorption sequence of aromatic compounds on selectivity

In selective hydrogenation of aromatic compounds, the first and key step is their adsorption on the catalyst surface. In competitive systems (e.g., mixtures of benzene, toluene, and xylene), the reaction pathway and its selectivity largely depend on the adsorption balance.

Alkyl-substituted aromatic compounds, particularly xylene and ethylbenzene, interact more strongly with the surfaces of common supports and catalysts than benzene. This trend was, for example, confirmed by Nugraha et al., who studied the adsorption of the BTEX components (benzene, toluene, ethylbenzene, xylene) on the ZnO(100) surface using DFT calculations: they observed the adsorption order benzene < toluene < xylene, with the adsorption energy of ethylbenzene being close to that of toluene [58].

This tendency is observed not only for ZnO but also for various carbonaceous and porous materials used for BTEX adsorption: in most cases, the order xylene ≥ ethylbenzene > toluene > benzene is reported. This behavior is attributed to the fact that the introduction of bulky and polarizable alkyl groups into the aromatic ring enhances the aromatic–surface interaction [59, 60].

The introduction of alkyl substituents increases the electron density of the aromatic ring through a positive inductive effect. This enhances the molecule's donor ability, leading to an increase in the bonding energy with the surface. Furthermore, as the molecular weight and polarizability increase in the series benzene < toluene < xylene, the contribution of van der Waals interactions also rises. In modern models, these interactions are considered critically important for stabilizing the adsorbed layer on chemically active metals such as Pt or Pd. As a result, toluene adsorbs more strongly than benzene, while xylene, with two methyl groups, forms an even stronger interaction [61].

In contrast, if the aromatic ring contains electron-withdrawing groups (e.g., $–CF_3$, –CN, $–NO_2$, etc.), the electron density of the ring decreases, weakening its interaction with the metal. In such cases, the adsorption energy is significantly reduced, so the hydrogenation of these compounds proceeds slowly or may not occur at all. For aromatics with electron-donating groups, adsorption is only slightly weakened, but the ring remains capable of undergoing hydrogenation [62, 63].

Thus, there is a direct correlation between adsorption strength and hydrogenation activity: the more strongly an aromatic compound binds to the catalyst surface, the faster and more easily it is hydrogenated. Modern quantum-chemical and molecular modeling studies show that the introduction of different substituents into the aromatic ring significantly alters the electronic structure of the π-system and the distance to the surface, which in turn leads to substantial variations in the adsorption energy.

However, it cannot be unconditionally stated that stronger adsorption always leads to faster hydrogenation. Modern heterogeneous catalysis theory, particularly the Sabatier principle indicates that catalytic activity reaches a maximum at intermediate adsorption energies:

– If the substrate adsorbs too weakly, its surface concentration is insufficient, resulting in a low reaction rate;

– If adsorption is too strong, intermediate and final products cannot desorb, blocking active sites and temporarily deactivating the catalyst.

This concept is discussed in detail in recent reviews and theoretical studies, including the works of Medford et al. and Stratton et al., which demonstrate that there is a volcano-type relationship between adsorption energy and catalytic activity [64, 65]. Optimal cyclohexene yields of 50–60% at >90% benzene conversion can be achieved when the productive π/σ-configuration dominates over flat π-adsorption [66–68].

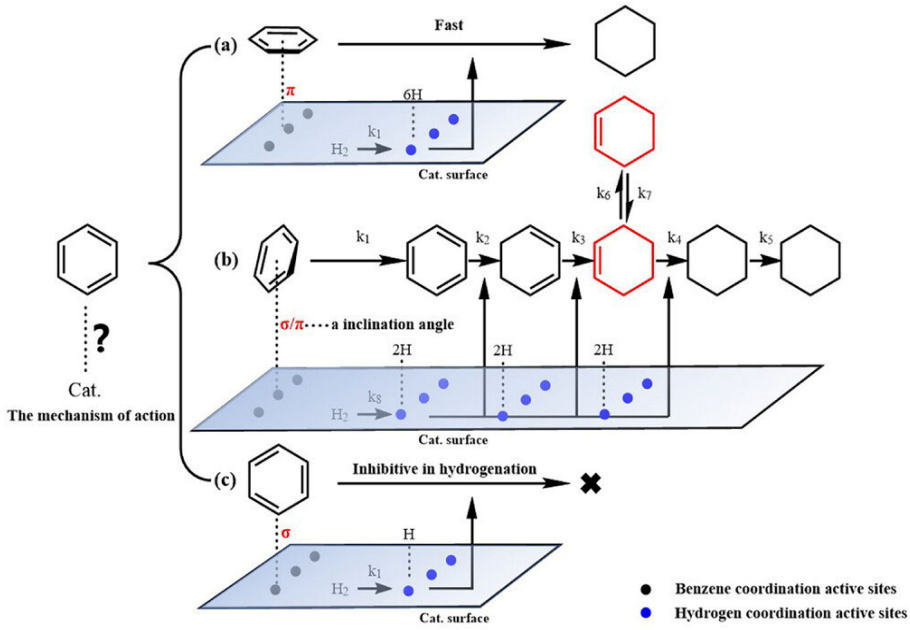

Fig. 5. Simultaneous reaction mechanisms in benzene hydrogenation. Reproduced with permission from Ref. [69].

Figure 5 illustrates the key concept of the parallel mechanism in benzene hydrogenation, explaining how the adsorption configuration of a benzene molecule on the surface of a Ru catalyst determines product selectivity. The diagram depicts three main modes of interaction between benzene and the active sites, each leading to different outcomes [69].

In configuration (a), benzene adsorbs parallel to the catalyst surface, forming π-bonds with the metal centers. This flat orientation allows the benzene molecule to be fully activated and surrounded by a large number of dissociated hydrogen atoms, enabling sequential sixfold hydrogen addition. As a result, a one-step full hydrogenation pathway occurs, producing cyclohexane at a high rate, but with low selectivity for cyclohexene.

Configuration (c) represents the opposite extreme-vertical σ-adsorption, where benzene binds to the surface only through σ-bonds. This orientation is essentially inactive in hydrogenation, as it blocks active sites without participating in the reaction, causing self-poisoning of the catalyst. While this form does not directly affect selectivity, it reduces overall activity due to the unproductive occupation of catalytic sites.

The most critical configuration for the selective synthesis of cyclohexene is the intermediate configuration (b), where the benzene molecule adsorbs at an angle, forming predominantly σ-bonds with weak π-interactions (π/σ-intermediate species). This distorted geometry allows benzene to react only with hydrogen atoms adjacent to the σ-bonds, leading to stepwise hydrogen addition and selective formation of cyclohexene. This is precisely the pathway that must be promoted to enhance selectivity.

The scheme emphasizes that all three adsorption modes can coexist in parallel, and their relative proportions depend on the electronic state of Ru (Ru^0 vs $Ru^{\delta+}$), the hydrophilicity of the catalyst, and hydrogen coverage. Modifiers such as Zn and La and a hydrophilic environment promote the formation of electron-deficient $Ru^{\delta+}$ sites, which weaken π-adsorption and self-poisoning, while simultaneously enhancing the prevalence of the productive π/σ configuration. A thick stationary layer of water on the hydrophilic surface accelerates the desorption of the poorly soluble cyclohexene, preventing its re-adsorption and further hydrogenation to cyclohexane.

Thus, in systems containing multiple aromatic compounds, the main factors influencing selectivity are:

- the order of adsorption (benzene is usually the weakest adsorbed);
- the geometry of binding (flat η^6-π complex versus tilted/σ-bound form);
- the effects of electronic and steric substituents.

In some systems, ethylbenzene and xylene adsorb more strongly on the catalyst surface than benzene and toluene, blocking active sites and significantly hindering the selective hydrogenation of benzene. This effect has been directly demonstrated in several studies after 2010 for Ni- and Pt-based catalysts during the hydrogenation of reformate gasoline and BTX fractions [70–73].

4.2. Influence of the reaction environment and pressure–temperature conditions

The selectivity of aromatic hydrogenation is simultaneously influenced by the reaction environment (gas or liquid phase), hydrogen pressure, and temperature. In systems containing multiple aromatic compounds (e.g., mixtures of benzene, toluene, and xylene or reformate gasoline), these effects are particularly pronounced, since adsorption balance, mass transfer, and chemical kinetics are interrelated and determine which aromatic component is hydrogenated first and to what extent.

In gas-phase hydrogenation, the aromatic compounds and H_2 usually flow as a vapor mixture through a stationary catalyst bed. Under these conditions, the partial pressure of each component can be precisely controlled. Recent LOHC reviews indicate that for hydrogenation of benzene to cyclohexane, an effective temperature range is 120–250 °C with pressures of 1–50 bar; similar conditions apply to the toluene → methylcyclohexane system [41, 74]. Within this range, increasing the partial pressure of hydrogen raises the coverage of the catalyst surface with *atomic hydrogen (H)**, limits prolonged adsorption of competing aromatics (e.g., toluene and xylene), and enhances the likelihood that the more weakly adsorbed benzene participates in the reaction.

In liquid-phase hydrogenation (trickle-bed, slurry, or autoclave modes), the aromatic compounds are dissolved in the liquid medium. In this case, the key limiting factors are the solubility and diffusion of hydrogen. At insufficient pressure, hydrogen cannot reach the catalyst surface in the required amount. As a result, the partial pressure of hydrogen at the catalyst surface in the liquid phase is lower than in the gas phase, and the degree of hydrogen coverage decreases. This enhances competitive adsorption of aromatics and reduces selectivity.

Recent process studies of LOHC systems describe the pathway of H_2 in the liquid phase as a three-step scheme [75, 76]:

1. Transfer of hydrogen from the gas phase into the liquid and its dissolution;

2. Diffusion of dissolved H_2 and aromatic molecules from the bulk liquid to the catalyst surface;

3. Adsorption–reaction–desorption steps on the catalyst surface.

At low hydrogen pressure or with insufficient mixing, the concentration of H_2 in the liquid is low, while the catalyst surface becomes highly covered with aromatics, intensifying competition for adsorption. In this situation, strongly adsorbing aromatic compounds (toluene, xylene, ethylbenzene) dominate the surface, displacing the more weakly adsorbed benzene. As a result, the hydrogenation of benzene slows down, and selectivity shifts toward the hydrogenation of the more strongly adsorbed aromatics [77–79].

In liquid-phase hydrogenation systems involving aromatic substrates, the reaction is commonly conducted under elevated hydrogen pressure and intensive stirring to improve hydrogen dissolution and transport to the catalyst surface. Studies on Ru-based benzene hydrogenation to cyclohexene [54, 80] and Rh/Rh–Au-catalyzed hydrogenation of benzene and toluene [55] show that the activity and conversion are strongly affected by hydrogen pressure, catalyst composition, and mass-transfer conditions. An increase in hydrogen availability at the catalyst surface enhances the concentration of dissolved H_2, reduces diffusion limitations, and improves substrate conversion. These results confirm the critical role of hydrogen mass transfer in three-phase liquid-phase hydrogenation systems.

Compared to the gas phase, in the liquid phase the solvent also plays an active role: its polarity, viscosity, and interactions with aromatics can alter the adsorption equilibrium on the catalyst surface [81, 82]. Studies of LOHC systems show that solvent choice significantly affects the rate and selectivity of dearomatization processes, and some aromatic solvents (e.g., benzene, toluene) can compete with other LOHC components for adsorption [83].

The hydrogen pressure and H_2/aromatic ratio are critical in both phases. Studies from 2018–2019 on Ni catalysts for the selective hydrogenation of benzene from reformate gasoline show that increasing hydrogen pressure and the H_2/aromatic ratio enhances benzene conversion, while the proper choice of support and metal loading improves benzene selectivity [70, 71]. At high pressure, the surface coverage with atomic hydrogen (H) increases*, and the effect of competing aromatics is relatively reduced, allowing even weakly adsorbed molecules like benzene to participate efficiently in the reaction.

The hydrogenation kinetics of benzene and toluene over a Pt/TiO_2 catalyst [84], as well as studies on the selective hydrogenation of benzene from gasoline fractions using Pt-based supports [85, 86], show that increasing pressure effectively removes benzene from gasoline.

The effect of temperature on hydrogenation selectivity is not merely a secondary factor relative to pressure; it has a direct influence. On one hand,

raising the temperature increases the chemical reaction rate and reduces diffusion limitations. On the other hand, because adsorption is exothermic, an increase in temperature reduces surface coverage by aromatics. Additionally, at high temperatures, side reactions such as cracking, isomerization, and dealkylation become more pronounced [56, 87, 88].

Reviews of LOHC systems and aromatic hydrogenation indicate that for hydrogenating aromatics such as benzene and toluene, the typical temperature range is 60–200 °C at 1–50 bar, with 80–150 °C considered a "mild regime" in most industrial projects. At temperatures above 200–250 °C, in addition to dearomatization, deep reforming and cracking processes are intensified [41, 89, 90].

Kinetic studies of benzene–toluene mixtures over Ni catalysts (130–190 °C, pressure of several to tens of bar) show that increasing the temperature raises the conversions of both benzene and toluene, but benzene selectivity passes through a maximum, which depends on the catalyst type and pressure [91, 92]. At too low temperatures, the overall reaction rate is limited, whereas at too high temperatures, hydrogenation of the more strongly adsorbed aromatics (e.g., toluene) becomes dominant, reducing benzene selectivity.

Thus, for the selective hydrogenation of benzene in the presence of other aromatics, the reaction medium, hydrogen pressure, and temperature must be considered as interrelated parameters. The gas phase allows precise control of partial pressures and easy management of surface H_2 coverage, whereas the liquid phase can limit selectivity due to mass-transfer effects and solvent interactions. Proper coordination of phase, pressure, H_2/aromatic ratio, and temperature enables the selective hydrogenation of benzene among competing aromatics, minimizes side reactions, and allows the development of an environmentally efficient process.

5. Catalysts for selective hydrogenation of benzene

Transition metals such as Ni, Pd, Pt, Ru, and Rh are traditionally used for benzene hydrogenation. On the surface of these metals, both hydrogen and benzene are simultaneously adsorbed, enabling the hydrogenation reaction. Each metal has its own advantages and limitations.

Nickel (Ni) is a relatively inexpensive and readily available transition metal, which makes it widely used in industry for benzene hydrogenation and the saturation of aromatic hydrocarbons. Although the catalytic activity of nickel surfaces is lower than that of noble metals such as Pt, Pd, and Ru, its cost-effectiveness and availability make Ni-based systems economically attractive for processes involving full hydrogenation of benzene.

Over the past decade, Ni-based catalysts have been improved mainly through control of the support type, particle size, and electronic structure. Ni/Al_2O_3 catalysts are among the most widely used and well-studied industrial systems for hydrogenating benzene to cyclohexane in streams similar to reformate gasoline or extract raffinate. Typical reaction conditions are 120–200 °C and 1–5 MPa (up to 8 MPa in some systems), providing high benzene conversion [92, 93].

However, recent comparative studies indicate that the benzene selectivity of Ni/Al_2O_3 catalysts in competitive benzene–toluene mixtures is moderate and can be significantly improved by modifying the support. Peyrovi et al. tested Ni/SiO_2, Ni/SiO_2–Al_2O_3, and Ni/Al_2O_3 catalysts on a mixture simulating reformate gasoline and found that Ni/Al_2O_3 gave the highest benzene conversion (~100%), whereas maximum benzene selectivity (~75%) was achieved on Ni/SiO_2; the SiO_2–Al_2O_3 hybrid support exhibited intermediate properties [71, 72].

To enhance the sulfur tolerance of nickel catalysts and their stability against side reactions, hydroprocessing catalysts are widely used, in which Ni is combined with Mo or W in sulfide form (NiMoS, NiWS). These systems typically operate at 300–380 °C and 5–15 MPa, enabling the simultaneous hydrogenation of polyaromatic compounds in heavy gas oils and pyrolysis fuels, as well as the removal of sulfur- and nitrogen-containing compounds through hydrodesulfurization and hydrodenitrogenation processes [94].

Kuchinskaya et al. demonstrated that nanosized Ni–W sulfide particles formed in situ on zeolite supports exhibit high activity in the hydrocracking of pyrolysis fuel into BTX fractions [95]. Such sulfide systems are primarily important for the combined hydrogenation and hydroprocessing of heavy fractions containing sulfur compounds and polycyclic aromatics rather than for the hydrogenation of benzene as an individual substrate.

Palladium (Pd) and platinum (Pt) are among the most active metals for the hydrogenation of aromatic compounds, including benzene. The d-orbitals of these noble metals interact effectively with the π-system of aromatics, facilitating the adsorption of both hydrogen and benzene. This allows them to achieve high hydrogenation rates at relatively low temperatures and pressures. Recent stud-

ies on benzene removal from reformate gasoline show that Pd and Pt supported on SiO_2, SiO_2–Al_2O_3, and Al_2O_3 exhibit high activity, achieving significant benzene conversion in the range of approximately 150–200 °C [73].

Platinum-based catalysts (Pt/Al_2O_3, Pt/zeolites) are considered classical industrial systems for the hydrogenation and/or hydroisomerization of benzene-containing gasoline fractions. For example, bimodal Pt/Al_2O_3–BEA catalysts were studied on a model mixture of 20% benzene + 80% n-heptane for benzene fraction processing, demonstrating that the high activity of Pt can be combined with the isomerization properties of the acidic support [96]. However, in competitive benzene–toluene mixtures, Pt catalysts usually hydrogenate both aromatic components simultaneously, so benzene selectivity is limited. This is due to the high intrinsic activity of the metal and the strong adsorption of toluene.

Palladium-based catalysts can exhibit a more favorable selectivity profile. In a classic study by Mashkovsky et al. on the competitive hydrogenation of a benzene–toluene (1:1) mixture, it was shown that Pd/Al_2O_3 exhibits significantly higher benzene selectivity compared to Pt/Al_2O_3 and Ni/Al_2O_3 systems. When the total pressure was increased to 37 atm, benzene hydrogenation selectivity reached approximately 76% [53]. This result indicates that on the palladium surface, the adsorption–desorption equilibrium of benzene combined with hydrogen solubility creates a more favorable environment for selective hydrogenation of benzene compared to the competing toluene.

Another important advantage of palladium is the ability to exploit spatial effects when combined with micro- and mesoporous structures. A 2019 study showed that a Pd/13X zeolite catalyst in a model benzene–n-heptane mixture at 200 °C and 1 MPa achieved ≈95% benzene conversion. This demonstrates not only the high activity of palladium, but also that the microporous structure of the zeolite allows benzene molecules to be adsorbed separately from larger components [97].

Pd and Pt systems on mesoporous supports such as FDU-12 and SiO_2–Al_2O_3 also show high activity for benzene removal from reformate gasoline, with Pd/FDU-12 in some cases exhibiting the best performance [73].

Because of the high cost of noble metals, Pd and Pt catalysts are typically used at low loadings or in bimetallic formulations that combine a noble metal with a less expensive 3d-transition metal or with a main-group promoter. Comparative studies of Pt–Co, Pt–Ni, Pt–Sn, and Pd–Pt systems for the hydrogenation of benzene and other aromatics show that tuning the surface composition allows effective control of both activity and selectivity. Rousset et al. compared monometallic Pt, Pd, and bimetallic Pd–Pt model catalysts on γ-Al_2O_3 in the hydrogenation of toluene and found that Pd–Pt particles exhibit turnover frequencies higher than those of either pure Pd or pure Pt, an effect attributed to electronic Pd–Pt interaction and to a more favourable hydrogen-coverage regime on the alloy surface [98]. Liu et al. reported that a Ru–Pt bimetallic catalyst supported on the MOF MIL-101(Cr) achieved more than 99% cyclohexane yield in the solvent-free hydrogenation of benzene, outperforming both monometallic Ru/MIL-101 and Pt/MIL-101 and a conventional Ru–Pt/activated-carbon reference [99]. In a benzene/toluene 1:1 mixture, Mashkovsky and co-workers demonstrated that the introduction of a second metal into Pd/Al_2O_3-based systems can shift the adsorption–desorption balance toward benzene, raising benzene selectivity to approximately 76% at 37 atm [53]. Bimetallic combinations of noble metals with main-group elements (Sn, In, Ga) provide an additional level of selectivity control: the electron-donating second metal partially blocks ensemble sites required for over-hydrogenation, decreasing the rate of consecutive saturation steps. In next-generation studies, particular attention is given to combining noble metals with nanostructured carbon materials (carbon nanotubes, graphene, N-doped carbons) and complex oxide systems, with precise tuning of the metal–support interface enabling controlled hydrogen activation and adjustment of the benzene adsorption–desorption equilibrium in the desired direction [99, 100].

Ruthenium (Ru)-based catalysts are among the most active systems for benzene hydrogenation and have been widely studied for both full hydrogenation (benzene → cyclohexane) and partial hydrogenation (benzene → cyclohexene). Recent studies indicate that Ru catalysts are among the most promising for hydrogenating benzene to cyclohexane: their activity is comparable to, and in some cases even exceeds, that of palladium and platinum, while the relatively lower cost of ruthenium makes them economically attractive.

The high activity of ruthenium is primarily due to its ability to efficiently dissociate H_2 molecules and form strongly adsorbed, highly reactive hydrogen species (H)* on the metal surface. Since the π-system of benzene interacts effectively with Ru surfaces, the stepwise hydrogenation of the ring proceeds

readily, enabling full hydrogenation to cyclohexane under favorable conditions within a short contact time.

In the full hydrogenation mode to cyclohexane, Ru catalysts can achieve complete benzene conversion at relatively low temperatures (≈60–120 °C) and moderate pressures (2–5 MPa). For example, several studies on nanosized Ru systems have shown that at 80 °C and 3 MPa, benzene can be hydrogenated to cyclohexane with high rate and high conversion (typically >95% benzene conversion within 60 min, with cyclohexane selectivity above 99%), highlighting the importance of high Ru dispersion and good metal surface accessibility [101].

Reviews covering 2018–2023 conclude that nanosized Ru catalysts (nanoparticles, hollow spheres, flake-like structures) exhibit exceptional activity and stability in the hydrogenation of aromatic compounds, including benzene.

A second important direction is the partial hydrogenation of benzene to cyclohexene, rather than to cyclohexane. In this process, ruthenium is often regarded as the most effective metal for selective hydrogenation. Studies from 2016–2018 on Ru–Zn catalysts and other promoted Ru systems have shown that cyclohexene yields can reach 50–60%. However, to suppress the thermodynamically favored full hydrogenation to cyclohexane, careful tuning of the catalyst's electronic structure, the metal–environment interface, and the composition of the liquid phase (water, salts, bases) is required [66–68].

For ruthenium-based catalysts, selectivity is strongly influenced by the reaction environment and modifiers. Water and hydroxide ions can adsorb on the Ru surface, hindering further hydrogenation of cyclohexene to cyclohexane, while the presence of promoters such as Zn, Mn, B, as well as alkaline and salt additives (e.g., NaOH, $ZnSO_4$), helps stabilize the benzene → cyclohexene step and enhances selectivity. These effects have been examined in detail in recent mechanistic studies [66, 68, 102].

Recent reviews on LOHC systems also highlight Ru catalysts as highly active and stable for hydrogen uptake and release cycles in benzene–cyclohexane pairs and other aromatic–naphthene systems. In terms of hydrogen release/uptake kinetics and thermal stability, Ru-based catalysts provide more balanced performance compared to Ni and some Pt/Pd systems.

Ru catalysts in full hydrogenation mode can hydrogenate benzene to cyclohexane at very high rates under relatively mild conditions, while in partial hydrogenation mode, with appropriate promoters and reaction environment tuning, they can achieve high selectivity toward cyclohexene. Compared to Ni-based systems, Ru generally exhibits higher activity, and compared to Pt/Pd systems, it offers greater flexibility in controlling selectivity toward intermediates such as cyclohexene, placing it in a distinctive position among modern catalysts for selective hydrogenation.

Table 1 summarizes the main types of catalysts used for benzene hydrogenation, including their operating conditions, selectivity, advantages, and limitations [66–68, 72, 73, 92–97, 101, 102]. The table shows that, compared to classical systems such as Ni/Al_2O_3, Pd/Al_2O_3 and Pd/13X catalysts can achieve higher benzene selectivity in benzene–toluene or benzene–n-heptane mixtures. Meso- and microporous supports (zeolites, FDU-12) provide additional spatial selectivity through adsorption hierarchy effects. Ru-based catalysts exhibit exceptionally high activity: under standard conditions, they almost completely hydrogenate benzene to cyclohexane. When modified with promoters (Zn, alkaline environment, salts), they can significantly enhance selectivity for partial hydrogenation to cyclohexene. Thus, the table allows a comparative evaluation of benzene hydrogenation catalysts and helps identify the most promising systems in terms of selectivity and economic efficiency for further research.

5.1. Stability and deactivation of catalysts in benzene hydrogenation

Long-term operational stability is a critical performance criterion that, alongside activity and selectivity, ultimately determines the practical viability of a benzene-hydrogenation catalyst. Under industrial conditions, catalysts gradually lose activity through several well-documented deactivation pathways: (i) thermal sintering of the active metal phase, particularly relevant for highly dispersed noble-metal catalysts under elevated-temperature conditions; (ii) carbonaceous deposition (coking) caused by oligomerisation of aromatic intermediates on Brønsted-acid sites of zeolitic or amorphous silica-alumina supports; (iii) poisoning by trace sulfur, nitrogen, or chlorine impurities present in reformate and pyrolysis-naphtha feedstocks, which is particularly severe for Pd and Pt; and (iv) leaching of the active metal under liquid-phase conditions, which is especially problematic for Ru-based systems in aqueous slurry reactors used for the partial hydrogenation to cyclohexene [103].

Table 1. Comparative characteristics of catalysts for selective benzene hydrogenation

Catalyst	Reaction medium/ feed mixture	Hydrogenation conditions (T, °C/p)	Main selectivity/result	Advantages	Disadvantages	Source
Ni/Al_2O_3	Reformate, benzene-enriched gasoline fractions	120–200 °C, 1–5 MPa (sometimes up to 8 MPa)	Benzene conversion ≈99–100%; in benzene–toluene mixture, benzene selectivity ≈50–55%	Low cost, widely used in industry, high catalytic activity	Limited benzene selectivity in the presence of competing aromatics	[92, 93]
Ni/SiO_2	Benzene–toluene (model reformate)	–	Benzene conversion ≈65–70%; benzene selectivity ≈75%	Higher selectivity due to inert support	Lower conversion compared with Ni/Al_2O_3; limited mechanical strength	[71, 72]
$Ni/SiO_2–Al_2O_3$	Benzene–toluene	120–200 °C, 1–5 MPa	Benzene conversion ≈85%; benzene selectivity ≈60%	Possibility to balance acid–base properties of the support	No pronounced advantages; “compromise” catalytic system	[71, 72]
NiMoS, NiWS (zeolite/Al_2O_3 etc.)	Heavy gas oils, pyrolysis fuels, aromatic compounds containing S and N	300–380 °C, 5–15 MPa	Aromatic conversion >90%; HDS efficiency >95%	Sulfur tolerance; comprehensive purification of heavy feedstocks	High temperature and pressure; lack of narrow benzene selectivity	[94, 95]
Pd/Al_2O_3, Pd/SiO_2, Pt/Al_2O_3, $Pt/SiO_2–Al_2O_3$	Reformate, benzene-containing gasoline	423–473 K (≈150–200 °C)	Benzene conversion >95% at 150–200 °C; benzene selectivity over Pt typically ≤50%	High intrinsic activity of noble metals; mild operating conditions	High cost; limited selectivity due to parallel hydrogenation of other aromatics	[73]
Pt/Al_2O_3–BEA	Model mixture: 20% benzene + 80% n-heptane	–	Benzene conversion ≈90%; n-heptane isomer yield ≈30–40%	Bifunctional catalyst increasing the octane number	Limited benzene selectivity in the benzene–toluene system; high cost of Pt	[96]
Pd/zeolite 13X	Model benzene–n-heptane mixture	200 °C, 1 MPa	Benzene conversion ≈90–95% at 200 °C, 1 MPa; activity drops to ≈81% after 20 h	High conversion at low pressure; spatial (shape) selectivity	Sensitivity to diffusion limitations; possible pore blockage by heavy components	[97]
Pd/Al_2O_3	Benzene–toluene (1:1)	Pressure up to 37 atm	Benzene conversion ≈40% at 37 atm; benzene selectivity ≈76 %	Good benzene selectivity in a competitive system; pressure tuning possible	Noble metal; high pressure required; possible poisoning during long-term operation	[53]
Pd/FDU-12 and other mesoporous Pd, Pt catalysts	Benzene removal from reformate	Mild hydrogenation conditions	Benzene conversion ≈98%; benzene selectivity ≈65–70%	Improved diffusion, high metal dispersion	Strong dependence of selectivity on the reaction system; high cost of noble metals	[101]
Ru (nanostructured)	Mainly liquid-phase benzene and model mixtures	60–120 °C, 2–5 MPa	Benzene conversion >99% at 80–120 °C, 2–5 MPa; cyclohexane selectivity >99%	Efficient dissociative adsorption of H_2; relatively cheaper noble metal; mild conditions	Difficult to suppress deep hydrogenation; precise tuning required for cyclohexene selectivity	[66–68, 101, 102]
Promoted Ru (Ru–Zn, Ru + NaOH, $ZnSO_4$ etc.)	Selective partial hydrogenation of benzene in liquid phase	Mild conditions; T and p depend on the author	Benzene conversion 60–80%; cyclohexene yield 50–60%	Strong increase in cyclohexene selectivity due to proper choice of medium and promoters	Very high sensitivity of the system; small changes in conditions again lead to complete hydrogenation	[66–68, 102]

Quantitative time-on-stream data illustrate the magnitude of these effects. For example, Alimohammadi and Fatthi reported that benzene conversion over a Pd/13X catalyst decreased from ≈90% to ≈81% over 20 h on stream at 200 °C and 1 MPa, while a Pd/Al_2O_3 reference catalyst showed a more gradual decline of less than 5% under the same conditions [104]. Hydrotreating Ni-Mo-W sulfide systems used in deep dearomatisation operate for several thousand hours but require periodic regeneration through controlled oxidation–sulfidation cycles to remove coke and restore the active sulfide phase. At 320–360 °C and 5–10 MPa, these systems achieve aromatic conversion >90% with simultaneous hydrodesulfurisation efficiency >95% [94, 95, 105]. For Ru-based partial-hydrogenation catalysts, the literature indicates that the addition of Zn, B, or alkaline modifiers not only improves cyclohexene selectivity but also markedly enhances stability by suppressing Ru particle agglomeration and stabilising the surface oxidation state of Ru in the $Ru^{\delta+}$ form [66–68, 102].

Several strategies have been developed to extend catalyst lifetime: (1) the use of bimetallic and trimetallic formulations (e.g., Pt–Pd, Pt–Sn, Ru–Pt), in which the second metal modifies the electronic structure and reduces the rate of carbon deposition [99, 100]; (2) confinement of metal nanoparticles within microporous or mesoporous supports (zeolites, MOFs, ordered mesoporous silicas), which physically restricts particle migration and sintering [96, 97, 99]; (3) controlled tuning of support acidity to balance the rate of hydrogenation against the rate of side reactions (cracking, transalkylation, isomerisation) that produce coke precursors [72, 106]; and (4) the use of natural and carbon-based supports with low intrinsic acidity (activated carbon, diatomite, modified bentonite), which inherently reduce coking [107–110]. Overall, the combined optimisation of activity, selectivity, and stability remains the principal challenge for the rational design of next-generation benzene-hydrogenation catalysts.

6. Supports and their influence

The support material determines the catalyst structure, the degree of metal particle dispersion, surface properties, and the nature of the metal–support interaction. Therefore, analyzing the structural, surface, acidic, and electronic characteristics of various supports and understanding their influence on activity and selectivity in benzene hydrogenation is of fundamental importance. Figure 6 presents a general overview of the types of supports used in catalytic benzene hydrogenation and their main advantages.

6.1. Classical supports

γ-Al_2O_3 (gamma-alumina), SiO_2 (silicon dioxide), TiO_2 (titanium dioxide), ZrO_2 (zirconium dioxide), and zeolites (e.g., Y-zeolite and ZSM-5) are widely used as supports for benzene hydrogenation catalysts. These materials differ in their porous structure, specific surface area, and the nature of acidic sites, which in turn affects the formation and performance of the metal particles in different ways. Figure 7 shows the structural formulas of the most widely used classical supports – (a) γ-alumina, (b) titanium dioxide, and (c) a representative aluminosilicate zeolite framework.

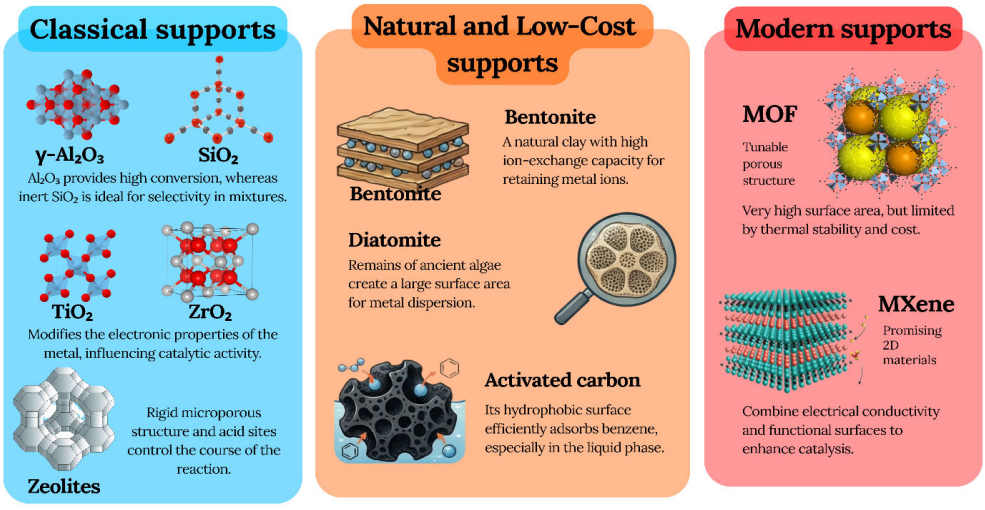

Fig. 6. Classification of catalyst supports used in benzene hydrogenation.

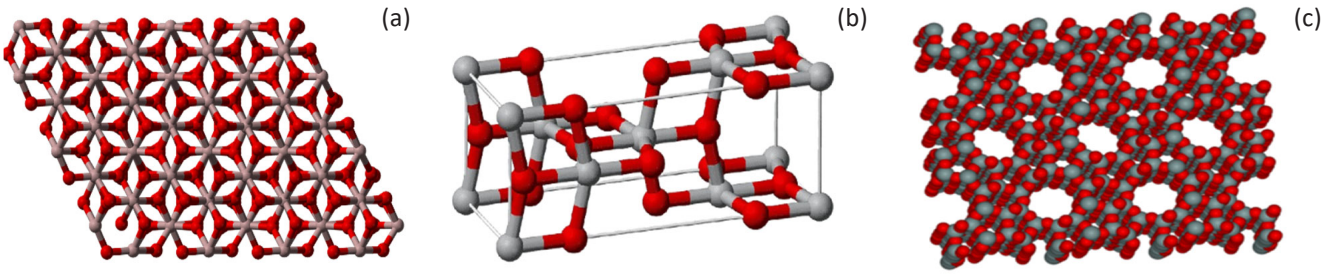

Fig. 7. Structural formulas of alumina (a), titanium oxide (b), and zeolite (c).

Alumina (Al_2O_3) is a widely used support characterized by a high specific surface area and moderate acidity. Silicon dioxide (SiO_2) is a chemically inert material with very low acidity and a high surface area. Studies have show that, in nickel-based catalysts, an Al_2O_3 support ensures a high degree of metal dispersion, leading to increased benzene conversion. For instance, a Ni/Al_2O_3 catalyst at 130 °C can achieve benzene conversion up to 99%, indicating that the porous structure of alumina promotes a uniform distribution of Ni nanoparticles and increases the number of active sites [72].

At the same time, nickel supported on SiO_2 (Ni/SiO_2) exhibits slightly lower activity in benzene hydrogenation. However, due to its inert and almost non-acidic surface, it demonstrates high selectivity in multicomponent mixtures. Specifically, in the hydrogenation of a benzene–toluene mixture, the Ni/SiO_2 catalyst selectively hydrogenated benzene while largely suppressing toluene hydrogenation, achieving benzene selectivity of up to 75% [72]. According to the authors, the decisive factor in this process was the pore size of the support, while its acidity and metal dispersion had much less influence. Thus, a more open porous structure (as in SiO_2) creates favorable conditions for adsorption and diffusion of larger molecules and, under certain conditions, enables selective hydrogenation of benzene.

Titanium dioxide (TiO_2) and zirconium dioxide (ZrO_2) are characterized by a pronounced strong metal–support interaction (SMSI) effect. When TiO_2 is reduced at high temperatures, an oxygen-deficient layer can form on its surface, partially covering the metal particles and giving rise to the SMSI effect. This alters the accessibility of the metal surface and its electronic density, directly influencing catalytic activity. For instance, in noble-metal/TiO_2 systems, it has been reported that after intensive reduction, the metal surface can be partially encapsulated by a protective titanium oxide layer, which decreases the activity in benzene hydrogenation [111]. At the same time, under moderate reduction conditions, Ru/TiO_2 catalysts have been shown to allow unhindered H_2 adsorption, meaning that the SMSI effect is not fully realized [112].

Zirconium dioxide (ZrO_2) is a stable, amphoteric support whose surface contains both acidic and basic sites, and it exhibits high chemical stability in both oxidative and reductive environments. By controlling the crystalline phase of ZrO_2 (monoclinic or tetragonal), it is possible to adjust the concentration of surface hydroxyl groups and its acid–base properties, making this material particularly promising as a catalyst support. Recent studies have shown that a biphasic (monoclinic–tetragonal) heterostructure of ZrO_2 enhances the performance of Ru-based catalysts in the selective hydrogenation of benzene. It is suggested that such a mixed-phase support forms surfaces with differing hydrophilicity: one phase is strongly hydrophilic, while the other is relatively less so. At the heterogeneous interface between these phases, a thin water layer forms, facilitating rapid desorption of the product–cyclohexene–from the Ru particle surface [113].

Zeolites (Y, ZSM-5) are aluminosilicate materials with a well-defined porous structure and strong acidic sites. In benzene hydrogenation reactions, zeolites can create a dual (bifunctional) environment: substrate molecules are adsorbed and concentrated within their micropores, while acidic sites such as H^+ can polarize the aromatic ring, thereby facilitating its hydrogenation on the metal centers. Moreover, the pore size of the zeolite significantly affects the reaction selectivity. For example, comparisons between Pt/ZSM-5 and Pt/Y catalysts have shown that the type of zeolite and its pore volume play a decisive role in determining selectivity [106].

The Pd/13X catalyst, based on a large-pore faujasite-type zeolite (Y-type, also designated as 13X), demonstrated higher benzene conversion in hydrogenation compared with Pd/Al_2O_3 and Pd/ZSM-5, reaching approximately 90% conversion at 200 °C and 1 MPa. The authors attribute this performance to the wider micropores of the 13X zeolite and its favorable surface properties, which facilitate the access and adsorption of benzene molecules onto the

Pd particles. However, it was noted that the activity of Pd/13X decreased from the initial 90% to 81% over 20 h, indicating more pronounced deactivation compared with the Al_2O_3-based catalyst; nonetheless, even after 20 h, the Pd/13X activity remained higher than that of other samples [104]. For the Pd/ZSM-5 catalyst, despite lower benzene conversion, the strong acidic sites of the support under certain conditions can promote additional isomerization or side reactions, meaning that careful optimization of reaction conditions and time is required when using this zeolite support.

Silicon dioxide (SiO_2), also referred to as amorphous silica, is one of the most widely used catalyst supports because of its chemical inertness, low intrinsic acidity, high specific surface area (typically 200–800 $m^2 \cdot g^{-1}$), and tunable pore structure ranging from non-porous fumed silica to ordered mesoporous variants (SBA-15, MCM-41, KIT-6, and FDU-12) [114]. The hydroxyl-rich silica surface (silanol groups, Si–OH) provides anchoring sites for the deposition of metal precursors via impregnation or grafting, allowing the formation of highly dispersed metal nanoparticles. The absence of strong Brønsted-acid sites makes SiO_2 particularly attractive when side reactions such as transalkylation, isomerisation, and cracking must be suppressed – a situation directly relevant to the selective hydrogenation of benzene in the presence of higher alkylaromatics, where preservation of the octane-boosting aromatic components is desirable. In Pt- and Pd-based catalysts, ordered mesoporous SiO_2 supports (SBA-15, MCM-41) have been shown to confine metal nanoparticles within the mesopore channels, providing both high dispersion and resistance against sintering, while their well-defined pore architecture imposes a degree of shape selectivity in the adsorption of competing aromatics [98, 115]. The principal limitations of SiO_2 are its moderate hydrothermal stability – extended exposure to water vapour at temperatures above 300–400 °C can lead to dehydroxylation and progressive collapse of the mesopore structure and the relative weakness of the metal–support interaction, which in some cases facilitates metal leaching under liquid-phase conditions.

6.2. Natural clay minerals as low-cost catalyst supports

Natural clay catalysts are inexpensive, abundant, and environmentally friendly materials used as supports in heterogeneous catalysis. Their porosity and tunable acidity allow effective dispersion of active metal species, enhancing catalytic activity and selectivity. Clays such as diatomite, montmorillonite, kaolinite, and bentonite can be modified by acid treatment, pillaring, or ion exchange to improve thermal stability and surface properties. They are widely applied in reactions such as hydrocarbon conversion, hydrogenation, and oxidation, as well as in environmental catalysis, due to their ability to provide both acidic functionality and structural support for metal nanoparticles, making them versatile and sustainable catalyst supports [107, 116–118].

Figure 8 shows SEM images of bentonite (a), diatomite (b), and activated carbon (c), illustrating their different surface morphologies. Bentonite exhibits a layered and flaky structure typical of clay minerals, in which plate-like particles are stacked together. Diatomite shows a characteristic cylindrical and highly ordered porous structure originating from fossilized diatom shells, with clearly visible regular pores that indicate high natural porosity. In contrast, activated carbon displays a highly developed porous and sponge-like surface with numerous irregular cavities and channels formed during the activation process, providing a large surface area and strong adsorption capacity. Overall, the images highlight significant differences in the texture and porosity of these materials, which influence their adsorption and catalytic properties.

Fig. 8. SEM images of bentonite [119] (a), diatomite [120] (b), and activated carbon [121] (c). Reproduced from Ref. [119–121]. Licensed under a Creative Commons Attribution (CC BY) license.

Bentonite is a natural clay whose main component is the mineral montmorillonite. Its crystalline structure is formed by alternating layers of silicon–oxygen tetrahedra and aluminum octahedra. Such a layered arrangement provides bentonite with a very large specific surface area and a pronounced anion–cation exchange capacity [122]. Various cations (Na^+, Ca^{2+}, etc.) are located in the interlayer space of the aluminosilicate sheets and can be easily replaced during ion-exchange processes. Owing to this property, bentonite can be readily impregnated with metal cations and used as a catalyst precursor: the metal ions are fixed within the clay layers and, upon subsequent reduction, form fine metallic particles uniformly distributed over the clay surface.

Another important feature of bentonite is its ability to swell in water and its high colloidal stability. The hydrophilic surface adsorbs a hydration shell and stabilizes the dispersion, which promotes the uniform distribution of the metal precursor during catalyst preparation. In addition, bentonite contains a significant number of –OH groups (located at the edges of the layers), which under certain conditions can act as acidic sites [123].

The use of bentonite as an inexpensive natural support has also been investigated in the field of selective benzene hydrogenation. For example, a Ru/bentonite catalyst was synthesized and studied for the partial hydrogenation of benzene to cyclohexene [124]. Ru nanoparticles introduced into purified bentonite by the impregnation method followed by hydrothermal treatment exhibited high catalytic activity: at 180 °C and an H_2 pressure of 5 MPa, significant benzene conversion was achieved. However, the yield of cyclohexene remained moderate at the initial stage [102]. Previous studies on Ru-based catalysts have shown that the addition of NaOH and $ZnSO_4$ can significantly enhance cyclohexene selectivity by modifying the hydrophilic and basic environment around Ru particles, thereby facilitating cyclohexene desorption and suppressing its further hydrogenation to cyclohexane [67, 68].

Diatomite is a sedimentary rock composed predominantly of silicon dioxide (approximately 90% SiO_2) and formed from the fossilized remains of ancient diatom algae. It is characterized by a powdery, highly porous structure that combines both micro- and macropores. Diatomite particles exhibit a distinctive morphology with numerous cavities and channels, resulting in a high specific surface area and well-developed porosity [125]. In addition, diatomite possesses high thermal stability and good chemical inertness due to its siliceous nature. Its highly porous structure and large surface area facilitate the dispersion of metal nanoparticles and improve the accessibility of active sites, making diatomite an attractive catalyst support for hydrogenation reactions [125, 126]. Using a diatomite support, benzene hydrogenation to cyclohexane has been performed in a plasma-assisted system at atmospheric pressure. The catalysts were prepared by impregnating the support with $Ni(NO_3)_2$ or $Cu(NO_3)_2$ solutions, followed by reduction. The authors reported benzene conversions exceeding 90% and cyclohexane selectivity greater than approximately 75% [126].

Activated carbon is a porous carbonaceous material characterized by an extremely high specific surface area and well-developed pore structure. Due to its chemical stability, hydrophobic surface, and tunable surface functionality, activated carbon is widely used as a catalyst support in hydrogenation reactions [108, 109]. The large internal surface area of activated carbon enables the stabilization of highly dispersed metal nanoparticles, which enhances the accessibility of active sites and improves catalytic performance in liquid-phase hydrogenation processes [110].

From the perspective of benzene hydrogenation, activated carbon is considered a promising catalyst support due to its high surface area, hydrophobic character, and chemical inertness. The hydrophobic surface promotes adsorption of aromatic compounds such as benzene, which is particularly advantageous in liquid-phase hydrogenation systems. In addition, carbon supports enable the stabilization of highly dispersed metal nanoparticles, often in the nanometer range, thereby increasing the accessibility of active sites and improving catalytic activity [108–110]. Unlike acidic oxide supports, activated carbon does not introduce strong acidic sites that may promote undesirable side reactions such as cracking or transalkylation; therefore, hydrogenation proceeds with higher selectivity toward saturated products. Ru nanoparticles supported on porous carbon materials have been reported to exhibit high hydrogenation activity under relatively mild conditions due to their small particle size and high dispersion [110].

6.3. Modern supports

Metal-organic frameworks (MOFs) are highly porous crystalline materials formed by coordination bonds between metal ions and organic ligands. A key advantage of MOFs is their tunable porous structure and functionality: the size and shape of

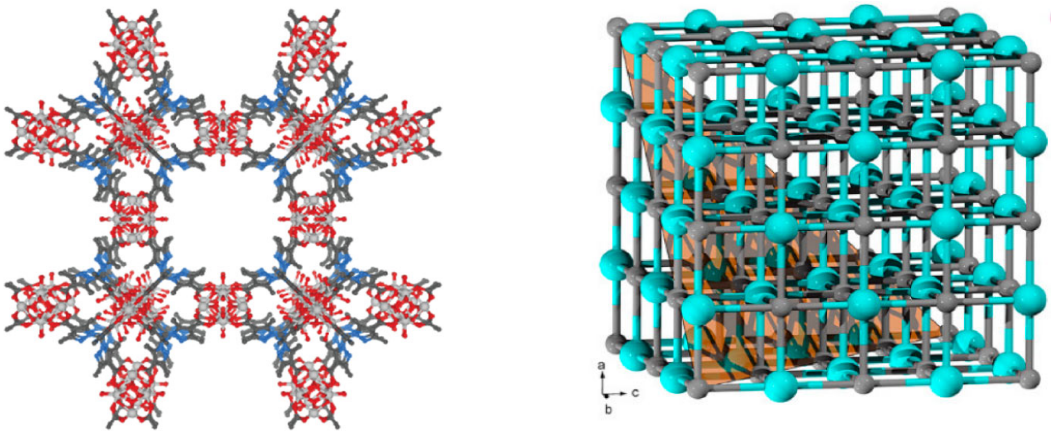

Fig. 9. Structures of MOF support (a) [35] and MXene support (b). Reproduced from Ref. [128]. Licensed under a Creative Commons Attribution (CC BY) licens.

the pores, as well as the surface chemistry, can vary significantly depending on the chosen ligand and metal cluster during synthesis [127]. In recent years, several studies have demonstrated the effectiveness of MOF-based supports in benzene hydrogenation reactions. For example, a bimetallic Ru–Pt catalyst deposited on the zeolite-like MOF MIL-101(Cr) showed high efficiency in benzene hydrogenation under solvent-free conditions. The catalyst developed by Liu et al., Ru–Pt/MIL-101, exhibited high activity for the complete hydrogenation of benzene to cyclohexane, outperforming the conventional Ru–Pt/activated carbon catalyst [99]. This high activity is attributed to the MOF's ability to stabilize small metal clusters, prevent their agglomeration, and adsorb benzene molecules, locally increasing their concentration.

It has also been reported that the Ru–B/MOF catalyst (ruthenium with boron additive on a MOF support), developed by Chinese researchers, achieved a cyclohexene yield of 24% at 180 °C and H_2 pressure of 5 MPa [129]. Although this value is still below the industrially required level, it clearly demonstrates the potential of MOF materials as supports. Distinctive features of MOFs include their high specific surface area, uniform micropores, and the ability to precisely modify the internal surface chemistry, allowing accurate control over the placement and state of metal particles. Moreover, some MOFs can exhibit bifunctional catalytic properties: for example, MOFs with acidic ligands can act as promoters themselves, facilitating the protonation of the aromatic benzene ring during hydrogenation. At the same time, MOFs have several limitations: not all structures are stable at elevated temperatures (decompose at 200–300 °C), and their large-scale synthesis remains expensive. For this reason, research on MOF supports is currently mostly confined to the laboratory scale.

MXenes are a class of two-dimensional materials that have seen rapid development in recent years. Their general formula is $M_{n+1}X_nT_x$, where M is a transition metal (Ti, V, Nb, etc.), X is carbon or nitrogen, and T_x represents surface functional groups (–O, –OH, –F, etc.). MXenes are obtained by selective etching of MAX phases (most often by dissolving the aluminum layer with acids), resulting in flat nanosheets with a thickness of just a few atomic layers. Characteristic features of MXenes include a combination of high electrical conductivity from the carbide–metal core with a hydrophilic, functionalized surface, as well as a large specific surface area [130, 131]. The presence of hydroxyl and oxygen-containing groups imparts acid–base properties to these materials.

MXene supports are particularly promising for hydrogen-involving reactions: their surfaces are favorable for H_2 adsorption and dissociation, and the close electronic interaction with deposited metal particles can lead to specific electronic effects. In recent years, MXene-based systems have been actively studied in selective benzene hydrogenation, not so much as standalone active phases, but as precursors for highly engineered supports. It has been shown that TiO_2 nanostructures derived from Ti_3C_2-MXene, used to achieve stable dispersion of Ru nanoparticles, provide high activity and selectivity in the partial hydrogenation of benzene to cyclohexene [132]. DFT calculations indicate that H_2 adsorption and dissociation on MXene surfaces are energetically favorable, and certain MXenes (e.g., Fe_2C, W_2N, and Mo_2C) can be considered promising platforms for hydrogenation reactions [133].

7. Conclusion

The analysis shows that catalytic hydrogenation of benzene remains one of the most challenging yet strategically important tasks in modern catalytic chemistry. The high thermodynamic stability of the aromatic ring, competitive adsorption in the presence of alkylated aromatics, and the process sensitivity to reaction conditions necessitate the precise tuning of catalytic systems. A comparison of different metals demonstrates that noble metals, primarily Pd and Pt, enable mild hydrogenation conditions but tend to promote the concurrent saturation of other aromatic compounds. Ruthenium holds a special position due to its combination of high activity and the ability to control the reaction pathway, ranging from complete hydrogenation of benzene to the selective formation of cyclohexene, depending on catalyst modification and the reaction environment.

It has been demonstrated that the support plays a role at least as important as that of the active metal: its porous structure, acid–base properties, and the nature of metal–support interactions significantly influence benzene adsorption, the stability of reaction intermediates, and the rate of product desorption. Zeolites and mesoporous materials enable spatial selectivity, whereas inert and carbon-based supports are effective in suppressing side reactions in liquid-phase systems. Natural and low-cost supports show considerable potential for the development of economically viable catalysts, provided that their surface chemistry is properly controlled. Furthermore, the future development of selective benzene hydrogenation processes is associated with a transition from empirical catalyst selection to the rational design of catalytic systems, grounded in a fundamental understanding of adsorption mechanisms, electronic effects, and mass transfer phenomena. Of particular interest are next-generation catalysts aimed at integrating de-aromatization processes with hydrogen storage systems, in which the benzene–cyclohexane pair is considered a promising component of hydrogen energy technologies. Thus, benzene hydrogenation remains not only a classical model reaction but also a versatile platform for the development of sustainable and environmentally oriented technologies of the future.

References

[1]. M.R. Rahimpour, M. Jafari, D. Iranshahi, Progress in catalytic naphtha reforming process: A review, *Appl. Energy* 109 (2013) 79–93. DOI: 10.1016/j.apenergy.2013.03.080

[2]. E.N. Al-Shafei, M.Z. Albahar, M.F. Aljishi, A. Akah, A.N. Aljishi, A. Alasseel, Catalytic conversion of heavy naphtha to reformate over the phosphorus-ZSM-5 catalyst at a lower reforming temperature, *RSC Adv.* 12 (2022) 25465–25477. DOI: 10.1039/D2RA04092A

[3]. Z. Wang, M. Ke, Z. Song, J. Li, J. Sun, Benzene reduction process simulation and optimization in catalytic cracking gasoline distillation, *Processes* 11 (2023) 151. DOI: 10.3390/pr11010151

[4]. F. Velázquez-Alonso, C.A. González-Ramírez, J.R. Villagómez-Ibarra, E.M. Otazo-Sánchez, M. Hernández-Juárez, et al., Operative improvement in the naphtha catalytic reforming process to reduce the environmental impact of benzene fugitive emissions from gasoline, *ChemEngineering* 9 (2025) 21. DOI: 10.3390/chemengineering9020021

[5]. S.R. Naqvi, A. Bibi, M. Naqvi, T. Noor, A.-S. Nizami, et al., New trends in improving gasoline quality and octane through naphtha isomerization: A short review, *Appl. Petrochem. Res.* 8 (2018) 131–139. DOI: 10.1007/s13203-018-0204-y

[6]. IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, Some Non-Heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures, International Agency for Research on Cancer, Lyon, 2010, p. 853. https://publications.iarc.who.int/110?utm.com

[7]. A.B. Patel, S. Shaikh, K.R. Jain, C. Desai, D. Madamwar, Polycyclic aromatic hydrocarbons: Sources, toxicity, and remediation approaches, *Front. Microbiol.* 11 (2020) 562813. DOI: 10.3389/fmicb.2020.562813

[8]. E. Dybing, P. E. Schwarze, P. Nafstad, K. Victorin, T. M. Penning, Polycyclic aromatic hydrocarbons in ambient air and cancer, Air Pollution and Cancer, 2013, p. 161.

[9]. P. Modisha, D. Bessarabov, Aromatic liquid organic hydrogen carriers for hydrogen storage and release, *Curr. Opin. Green Sustain. Chem*. 42 (2023) 100820. DOI: 10.1016/j.cogsc.2023.100820

[10]. C. Chu, K. Wu, B. Luo, Q. Cao, H. Zhang, Hydrogen storage by liquid organic hydrogen carriers: Catalyst, renewable carrier, and technology – A review, *Carbon Resour. Convers.* 6 (2023) 334–351. DOI: 10.1016/j.crcon.2023.03.007

[11]. L. Foppa, J. Dupont, Benzene partial hydrogenation: Advances and perspectives, *Chem. Soc. Rev.* 44 (2015) 1886–1897. DOI: 10.1039/C4CS00324A

[12]. W. Gu, M.M. Stalzer, C.P. Nicholas, A. Bhattacharyya, A. Motta, et al., Benzene selectivity in competitive arene hydrogenation: Effects of single-site catalyst·acidic oxide surface binding geometry, *J. Am. Chem. Soc.* 137 (2015) 6770–6780. DOI: 10.1021/jacs.5b03254

[13]. M.D. Garba, A. Galadima, Catalytic hydrogenation of hydrocarbons for gasoline production, *J. Phys. Sci.* 29 (2018) 153–176. DOI: 10.21315/jps2018.29.2.10

[14]. X. Li, W. Hao, N. Yi, Y.-M. He, Q.-H. Fan, Asymmetric transfer hydrogenation of naphthol and phenol derivatives with cooperative heterogeneous and homogeneous catalysis, *CCS Chem.* 5 (2023) 2277–2289. DOI: 10.31635/ccschem.023.202303007

[15]. X. Deng, J. Wang, N. Guan, L. Li, Catalysts and mechanisms for the selective heterogeneous hydrogenation of carbon-carbon triple bonds, *Cell Rep. Phys. Sci.* 3 (2022) 101017. DOI: 10.1016/j.xcrp.2022.101017

[16]. M.A. Stoffels, F.J.R. Klauck, T. Hamadi, F. Glorius, J. Leker, Technology trends of catalysts in hydrogenation reactions: A patent landscape analysis, *Adv. Synth. Catal.* 362 (2020) 1258–1274. DOI: 10.1002/adsc.201901292

[17]. M.O. Ivanytsya, V.V. Subotin, K.S. Gavrilenko, S.V. Ryabukhin, D.M. Volochnyuk, S.V. Kolotilov, Advances and challenges in development of transition metal catalysts for heterogeneous hydrogenation of organic compounds, *Chem. Rec.* 24 (2024) e202300300. DOI: 10.1002/tcr.202300300

[18]. J.R. Cabrero-Antonino, R. Adam, V. Papa, M. Beller, Homogeneous and heterogeneous catalytic reduction of amides and related compounds using molecular hydrogen, *Nat. Commun.* 11 (2020) 3893. DOI: 10.1038/s41467-020-17588-5

[19]. S. Wang, X. Lou, B. Liu, Probing heterolytic H2 dissociation on heterogeneous catalysts: A brief review of experimental strategies, *Processes* 13 (2025) 1465. DOI: 10.3390/pr13051465

[20]. M. Johansson, O. Lytken, I. Chorkendorff, The sticking probability for H2 on some transition metals at a hydrogen pressure of 1 bar, *J. Chem. Phys*. 128 (2008) 034706. DOI: 10.1063/1.2825296

[21]. J.A. Moulijn, P.W.N.M. van Leeuwen, R.A. van Santen, Chapter 4 Bonding and elementary steps in catalysis, *Stud. Surf. Sci. Catal.* 79 (1993) 89–158. DOI: 10.1016/S0167-2991(08)63808-2

[22]. H. Shen, H. Li, Z. Yang, C. Li, Magic of hydrogen spillover: Understanding and application, *Green Energy Environ.* 7 (2022) 1161–1198. DOI: 10.1016/j.gee.2022.01.013

[23]. K.G. Lakshmikanth, P.K. Ayishabi, R. Chatanathodi, Ab initio DFT studies of adsorption characteristics of benzene on close-packed surfaces of transition metals, *Comput. Mater. Sci.* 137 (2017) 10–19. DOI: 10.1016/j.commatsci.2017.05.019

[24]. M.F. Puthiyaparambath, R. Chatanathodi, Adsorption of benzene on defective Pt surfaces: A DFT study, *Surf. Sci.* 716 (2022) 121959. DOI: 10.1016/j.susc.2021.121959

[25]. R. Chatanathodi, Adsorption of benzene on low index surfaces of platinum in the presence of van der Waals interactions, *Surf. Sci.* 664 (2017) 8–15. DOI: 10.1016/j.susc.2017.05.009

[26]. H. Chen, J. Meng, X. Wang, S. Ma, C. Bu, et al., Insights into the adsorption and decomposition mechanisms of tar typical model compounds (benzene, toluene and phenol) on Ni(111) surface by DFT calculations, *J. Energy Inst.* 114 (2024) 101602. DOI: 10.1016/j.joei.2024.101602

[27]. M.K. Sabbe, G. Canduela-Rodriguez, M.-F. Reyniers, G.B. Marin, DFT-based modeling of benzene hydrogenation on Pt at industrially relevant coverage, *J. Catal.* 330 (2015) 406–422. DOI: 10.1016/j.jcat.2015.08.003

[28]. M. Saeys, J.W. Thybaut, M. Neurock, G.B. Marin, Kinetic models for catalytic reactions from first principles: Benzene hydrogenation, *Mol. Phys.* 102 (2004) 267–272. DOI: 10.1080/00268970410001668516

[29]. Y. Cui, N. Wang, J. Han, Z. Wang, M. Zhang, et al., Theoretical study on the effect of Pd/Zn ratio on benzene hydrogenation catalytic activity and selectivity, *Catalysts* 15 (2025) 57. DOI: 10.3390/catal15010057

[30]. N.T. Shikhverdieva, U.A. Mammedova, N.A. Zeynalov, The scientific basis of industrial application of the process of selective hydrogenation of benzene in different catalytic systems, *Azerbaijan Chemical Journal* 3 (2023) 39–52. DOI: 10.32737/0005-2531-2023-3-39-52

[31]. M.K. Sabbe, G. Canduela-Rodriguez, J.-F. Joly, M.-F. Reyniers, G.B. Marin, Ab initio coverage-dependent microkinetic modeling of benzene hydrogenation on Pd(111), *Catal. Sci. Technol*. 7 (2017) 5267–5283. DOI: 10.1039/C7CY00962C

[32]. H. He, R.J. Meyer, R.M. Rioux, M.J. Janik, Catalyst design for selective hydrogenation of benzene to cyclohexene through density functional theory and microkinetic modeling, *ACS Catal.* 11 (2021) 11831–11842. DOI: 10.1021/acscatal.1c02630

[33]. Z.Y. Hu, Z.-Z. He, L. Chen, C. Shang, Z.-P. Liu, In situ selective site-blocking dictates benzene partial hydrogenation to cyclohexene on Zn-promoted

Ru-based catalysts, *ACS Catal.* 15 (2025) 7015–7027. DOI: 10.1021/acscatal.5c00950

[34]. F. Xie, L. Chen, E.M. Cedeño Morales, S. Ullah, Y. Fu, et al., Complete separation of benzene-cyclohexene-cyclohexane mixtures via temperature-dependent molecular sieving by a flexible chain-like coordination polymer, *Nat. Commun*. 15 (2024) 2240. DOI: 10.1038/s41467-024-46556-6

[35]. C. Sun, Synthesis of Metal-Organic Frameworks and Crystalline Porous Polymers and Studies of Their Reactivity, PhD thesis, Massachusetts Institute of Technology, 2021, p. 119.

[36]. M. Saeys, M.-F. Reyniers, M. Neurock, G.B. Marin, Adsorption of cyclohexadiene, cyclohexene and cyclohexane on Pt(111), *Surf. Sci.* 600 (2006) 3121–3134. DOI: 10.1016/j.susc.2006.05.059

[37]. M. Vaštyl, Z. Jankovská, G.J.F. Cruz, L. Matějová, A case study on microwave pyrolysis of waste tyres and cocoa pod husk; effect on quantity and quality of utilizable products, *J. Environ. Chem. Eng.* 10 (2022) 106917. DOI: 10.1016/j.jece.2021.106917

[38]. C. Fan, Y.-A. Zhu, X.-G. Zhou, Z.-P. Liu, Catalytic hydrogenation of benzene to cyclohexene on Ru(0001) from density functional theory investigations, *Catal. Today* 160 (2011) 234–241. DOI: 10.1016/j.cattod.2010.03.075

[39]. D. Zhao, J. Meng, X. Lin, Mathematical modelling of simultaneous hydrogenation of benzene and ethane dehydrogenation in a membrane reactor, *Case Stud. Therm. Eng*. 71 (2025) 106133. DOI: 10.1016/j.csite.2025.106133

[40]. D.K. Verma, K. Des Tombe, Benzene in gasoline and crude oil: Occupational and environmental implications, *AIHA Journal* 63 (2002) 225–230. DOI: 10.1080/15428110208984708

[41]. R. Barthos, F. Lónyi, Y. Shi, Á. Szegedi, A. Vikár, et al., Catalytic aspects of liquid organic hydrogen carrier technology, *Catalysts* 15 (2025) 427. DOI: 10.3390/catal15050427

[42]. E. Dada, L. Achenie, Production of cyclohexane from hydrogenation of benzene using microreactor technology, *Comput. Aided Chem. Eng*. 31 (2012) 240–244. DOI: 10.1016/B978-0-444-59507-2.50040-8

[43]. F. Hao, J. Zhong, P.-L. Liu, K.-Y. You, C. Wei, et al., Preparation of mesoporous SiO2–Al2O3 supported Co or Mn catalysts and their catalytic properties in cyclohexane nitrosation to ε-caprolactam, *J. Mol. Catal. A: Chem*. 351 (2011) 210–216. DOI: 10.1016/j.molcata.2011.10.010

[44]. R.S. Suppino, R. Landers, A.J.G. Cobo, Partial hydrogenation of benzene on Ru catalysts: Effects of additives in the reaction medium, *Appl. Catal. A: Gen*. 452 (2013) 9–16. DOI: 10.1016/j.apcata.2012.11.034

[45]. Y. Ni, Z. Han, Y. Chai, G. Wu, L. Li, Catalytic hydrogen storage in liquid hydrogen carriers, *EES Catal.* 1 (2023) 459–494. DOI: 10.1039/D3EY00076A

[46]. G. Cabrera, M. Mora, J.P. Gil-Burgos, R. Visbal, F. Machuca-Martínez, E. Mosquera-Vargas, Liquid organic hydrogen carrier concepts and catalysts for hydrogenation and dehydrogenation reactions, *Molecules* 29 (2024) 4938. DOI: 10.3390/molecules29204938

[47]. L. Chen, P. Verma, K. Hou, Z. Qi, S. Zhang, et al., Reversible dehydrogenation and rehydrogenation of cyclohexane and methylcyclohexane by single-site platinum catalyst, *Nat. Commun*. 13 (2022) 1092. DOI: 10.1038/s41467-022-28607-y

[48]. G. Zhou, W. Liu, Y. Zhao, X. Wang, S. Chen, et al., Reversible hydrogenation and dehydrogenation of benzene for hydrogen storage on highly dispersed Pd/γ-Al2O3 catalyst, *J. Ind. Eng. Chem*. 134 (2024) 561–573. DOI: 10.1016/j.jiec.2024.01.018

[49]. G. Busca, Production of gasolines and monocyclic aromatic hydrocarbons: From fossil raw materials to green processes, *Energies* 14 (2021) 4061. DOI: 10.3390/en14134061

[50]. U.N. Otzhan, A.K. Kurmansitova, L.R. Sassykova, A.A. Serikkanov, A.S. Kenzhebekov, E.B. Starikov, Catalysts for selective hydrogenation of aromatic nitrocompounds and hydrocarbons, *Int. J. Biol. Chem*. 9 (2016) 40–44. DOI: 10.26577/2218-7979-2016-9-2-40-44

[51]. S.D. Lin, M.A. Vannice, Hydrogenation of aromatic hydrocarbons over supported Pt catalysts. I. Benzene hydrogenation, *J. Catal.* 143 (1993) 539–553. DOI: 10.1006/jcat.1993.1297

[52]. L.M. Kustov, A.L. Tarasov, A.L. Kustov, O.P. Tkachenko, Enhancement of efficiency of Pd/Al2O3 catalysts in selective hydrogenation of sec-butylbenzene by modification with H2SO4 or H2WO4, *Metals* 11 (2021) 281. DOI: 10.3390/met11020281

[53]. I.S. Mashkovsky, G.N. Baeva, A.Yu. Stakheev, T.V. Voskoboynikov, P.T. Barger, Pd/Al2O3 catalyst for selective hydrogenation of benzene in benzene–toluene mixture, *Mendeleev Commun*. 19 (2009) 108–109. DOI: 10.1016/j.mencom.2009.03.020

[54]. A.N. Manassova, K. Toshtay, Catalytic activity of supported ruthenium catalysts in the benzene hydrogenation reaction, *Neft i Gaz* 6 (2025) 293–304. DOI: 10.37878/2708-0080/2025-6.18

[55]. S. Konuspayev, M. Shaimardan, N. Annas, T.S. Abildin, Y.Y. Suleimenov, Hydrogenation of benzene and toluene over supported rhodium and rhodium-gold catalysts, *MATEC Web Conf.* 340 (2021) 01026. DOI: 10.1051/matecconf/202134001026

[56]. N. Cherkasov, S. Asano, Y. Tsuji, K. Okazawa, K. Yoshizawa, et al., Mechanistic origins of accelerated hydrogenation of mixed alkylaromatics by synchronised adsorption over Rh/SiO2, *React. Chem. Eng.* 8 (2023) 1341–1348. DOI: 10.1039/D3RE00032J

[57]. Z. Liu, I.A. Hamad, Y. Li, Y. Chen, S. Wang, et al., Poisoning and competitive adsorption effects during phenol hydrogenation on platinum in water-alcohol mixtures, *Appl. Catal. A: Gen*. 585 (2019) 117199. DOI: 10.1016/j.apcata.2019.117199

[58]. N. Nugraha, A.G. Saputro, M.K. Agusta, F.T. Akbar, A.D. Pramudya, Density functional study on benzene, toluene, ethylbenzene and xylene adsorptions on ZnO(100) surface, *Molekul* 14 (2019) 37. DOI: 10.20884/1.jm.2019.14.1.501

[59]. M. Kim, E. Myung, H. Kim, N. Choi, K. Cho, Aqueous benzene, toluene, ethylbenzene and xylene (BTEX) removal using core-shell structure activated carbon ball as a permeable reactive barrier material, *Results Eng*. 23 (2024) 102797. DOI: 10.1016/j.rineng.2024.102797

[60]. N. Baimatova, M. Derbissalin, A. Kabulov, B. Kenessov, Adsorption of benzene, toluene, ethylbenzene and o-xylene by carbon-based adsorbents, *Eurasian Chem.-Technol. J.* 18 (2016) 123–131. DOI: 10.18321/ectj433

[61]. W. Liu, V.G. Ruiz, G.-X. Zhang, B. Santra, X. Ren, et al., Structure and energetics of benzene adsorbed on transition-metal surfaces: Density-functional theory with van der Waals interactions including collective substrate response, *New J. Phys.* 15 (2013) 053046. DOI: 10.1088/1367-2630/15/5/053046

[62]. D. Duraczyńska, E.M. Serwicka, A. Drelinkiewicz, R.P. Socha, M. Zimowska, et al., Solvent and substituent effects in hydrogenation of aromatic ketones over Ru/polymer catalyst under very mild conditions, *Mol. Catal.* 470 (2019) 145–151. DOI: 10.1016/j.mcat.2019.04.003

[63]. D.P. Miller, S. Simpson, N. Tymińska, E. Zurek, Benzene derivatives adsorbed to the Ag(111) surface: Binding sites and electronic structure, *J. Chem. Phys*. 142 (2015) 101924. DOI: 10.1063/1.4908267

[64]. A.J. Medford, A. Vojvodic, J.S. Hummelshøj, J. Voss, F. Abild-Pedersen, et al., From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis, *J. Catal*. 328 (2015) 36–42. DOI: 10.1016/j.jcat.2014.12.033

[65]. S.M. Stratton, S. Zhang, M.M. Montemore, Addressing complexity in catalyst design: From volcanos and scaling to more sophisticated design strategies, *Surf. Sci. Rep.* 78 (2023) 100597. DOI: 10.1016/j.surfrep.2023.100597

[66]. H. Sun, Z. Chen, L. Chen, H. Li, Z. Peng, et al., Selective hydrogenation of benzene to cyclohexene over Ru-Zn catalysts: Investigations on the effect of Zn content and ZrO2 as the support and dispersant, *Catalysts* 8 (2018) 513. DOI: 10.3390/catal8110513

[67]. H. Sun, Z. Chen, C. Li, L. Chen, Z. Peng, et al., Selective hydrogenation of benzene to cyclohexene over Ru-Zn catalysts: Mechanism investigation on NaOH as a reaction additive, *Catalysts* 8 (2018) 104. DOI: 10.3390/catal8030104

[68]. H. Sun, Z. Chen, C. Li, L. Chen, Y. Li, et al., Selective hydrogenation of benzene to cyclohexene over monometallic Ru catalysts: Investigation of ZnO and ZnSO4 as reaction additives as well as particle size effect, *Catalysts* 8 (2018) 172. DOI: 10.3390/catal8050172

[69]. X. Cheng, Y. He, Y. Zhu, Z. Wu, S. Li, et al., Partial hydrogenation of benzene to cyclohexene: A review for Ru-based catalyst design, *ChemCatChem* 17 (2025) e202401562. DOI: 10.1002/cctc.202401562

[70]. T. Rostamikia, N. Parsafard, M.H. Peyrovi, Benzene reduction in reformate gasoline by competitive hydrogenation: Effect of the preparation method, *ChemistrySelect* 4 (2019) 4861–4866. DOI: 10.1002/slct.201900278

[71]. M.H. Peyrovi, N. Parsafard, Competitive hydrogenation of benzene in reformate gasoline over Ni supported on SiO2, SiO2–Al2O3, and Al2O3 catalysts: Influence of support nature, *Energy Fuels* 32 (2018) 11432–11439. DOI: 10.1021/acs.energyfuels.8b02952

[72]. M.H. Peyrovi, N. Parsafard, Z. Mohammadian, Benzene selective hydrogenation over supported Ni (nano-) particles catalysts: Catalytic and kinetics studies, *Chin. J. Chem. Eng*. 26 (2018) 521–528. DOI: 10.1016/j.cjche.2017.05.022

[73]. T. Rostamikia, N. Parsafard, M.H. Peyrovi, Pd and Pt supported on mesoporous silica, silica–alumina and alumina as catalysts for benzene elimination in reformate gasoline, *React. Kinet. Mech. Catal.* 127 (2019) 345–356. DOI: 10.1007/s11144-019-01562-4

[74]. S. Ramadhani, Q.N. Dao, Y. Imanuel, M. Ridwan, H. Sohn, et al., Advances in catalytic hydrogenation of liquid organic hydrogen carriers (LOHCs) using high-purity and low-purity hydrogen, *ChemCatChem* 16 (2024) e202401278. DOI: 10.1002/cctc.202401278

[75]. A. García, P. Marín, S. Ordóñez, Hydrogenation of liquid organic hydrogen carriers: Process scale-up, economic analysis and optimization, *Int. J. Hydrog. Energy* 52 (2024) 1113–1123. DOI: 10.1016/j.ijhydene.2023.06.273

[76]. P. Rango, F. Cuevas, Hydrogen Storage: A Wide Range of Solutions, Wiley-ISTE, 2025, p. 416. DOI: 10.1002/9781394401635

[77]. M.Ş. Ece, S. Kutluay, Comparative and competitive adsorption of gaseous toluene, ethylbenzene, and xylene onto natural cellulose-modified Fe3O4 nanoparticles, *J. Environ. Chem. Eng*. 10 (2022) 107389. DOI: 10.1016/j.jece.2022.107389

[78]. S.M. Yakout, A.A.M. Daifullah, Adsorption of toluene, ethylbenzene and xylenes by activated carbon-impact of molecular oxygen, *Desalin. Water Treat.* 52 (2014) 4977–4981. DOI: 10.1080/19443994.2013.821028

[79]. M. Wu, Z. Zhao, G. Cai, C. Wang, G. Cheng, X. Wang, Adsorption behaviour and mechanism of benzene, toluene and m-xylene (BTX) solution onto kaolinite: Experimental and molecular dynamics simulation studies, *Sep. Purif. Technol.* 291 (2022) 120940. DOI: 10.1016/j.seppur.2022.120940

[80]. H. Sun, S. Li, Y. Zhang, H. Jiang, L. Qu, et al., Selective hydrogenation of benzene to cyclohexene in continuous reaction device with two reaction reactors in series over Ru-Co-B/ZrO2 catalysts, *Chin. J. Catal*. 34 (2013) 1482–1488. DOI: 10.1016/S1872-2067(12)60637-8

[81]. S. Zhao, J. Cai, H. Chen, J. Shen, Understanding the effects of solvents on the hydrogenation of toluene over supported Pd and Ru catalysts, *Catal. Commun.* 157 (2021) 106330. DOI: 10.1016/j.catcom.2021.106330

[82]. J. Li, Y. Xi, Y. Qiao, Z. Zhao, J. Liu, F. Li, Solvent effects on heterogeneous catalysis for the selective hydrogenation, *ChemCatChem* 16 (2024) e202400120. DOI: 10.1002/cctc.202400120

[83]. B.L. Tran, M.E. Bowden, T. Autrey, M.Y. Byun, K. Müller, Roles of solvent in the catalytic hydrogen release from liquid organic hydrogen carriers: Chemical, thermodynamical and technological aspects, *Top. Catal.* 67 (2024) 892–899. DOI: 10.1007/s11244-024-01950-8

[84]. R.V. Kazantsev, N.A. Gaidai, N.V. Nekrasov, K. Tenchev, L. Petrov, A.L. Lapidus, Kinetics of benzene and toluene hydrogenation on a Pt/TiO2 catalyst, *Kinet. Catal*. 44 (2003) 529–535. DOI: 10.1023/A:1025194117868

[85]. K. Goundani, C. Papadopoulou, C. Kordulis, Benzene elimination from reformate gasoline by high pressure hydrogenation in a fixed-bed reactor, *React. Kinet. Catal. Lett*. 82 (2004) 149–155. DOI: 10.1023/B:REAC.0000028816.68260.6b

[86]. A. Massenova, M. Kalykberdiyev, A. Sass, N. Kenzin, A. Ussenov, et al., Catalytic technologies for solving environmental problems in the production of fuels and motor transport in Kazakhstan, *Catalysts* 10 (2020) 1197. DOI: 10.3390/catal10101197

[87]. S. Akmaz, P.A. Caglayan, Effect of catalyst, temperature, and hydrogen pressure on slurry hydrocracking reactions of naphthalene, *Chem. Eng. Technol*. 38 (2015) 917–930. DOI: 10.1002/ceat.201400300

[88]. A. Fischer, Toluene hydrogenation on Pt nanoparticles: Site-ensemble requirements and inverse temperature effects on rates, *J. Catal.* 454 (2026) 116574. DOI: 10.1016/j.jcat.2025.116574

[89]. E. Rakić, M. Grilc, B. Likozar, Liquid organic hydrogen carrier hydrogenation–dehydrogenation: From ab initio catalysis to reaction micro-kinetics modelling, *Chem. Eng. J*. 472 (2023) 144836. DOI: 10.1016/j.cej.2023.144836

[90]. A.B. German Rodrigo, New Technology for Hydrogenation Processes in the Alimentary Industry, PhD thesis, University of Valladolid, Spain, 2025, p. 157.

[91]. B. Kedelbaev, K. Lakhanova, G. Iztleuov, S. Turabdzhanov, Research of the process of continuous hydrogenation of benzene in the presence of modified catalysts, *Technical Science and Innovation* 2021 (2021) 36–44. https://btstu.researchcommons.org/journal/vol2021/iss1/1/

[92]. Z. Mohammadian, N. Parsafard, Optimization of kinetic study by response surface methodology on the various types Ni supported catalysts in competitive benzene hydrogenation, *Theor. Found. Chem. Eng.* 56 (2022) 1179–1188. DOI: 10.1134/S0040579522330053

[93]. R. Molina, G. Poncelet, Hydrogenation of benzene over alumina-supported nickel catalysts prepared from Ni(II) acetylacetonate, *J. Catal.* 199 (2001) 162–170. DOI: 10.1006/jcat.2001.3169

[94]. S. Albersberger, Understanding and Controlling Properties of Bulk Ni-Mo-W Sulfides for Hydrodefunctionalization, PhD thesis, Technische Universität München, 2019, p. 225.

[95]. T. Kuchinskaya, M. Kniazeva, V. Samoilov, A. Maximov, In situ generated nanosized sulfide Ni-W catalysts based on zeolite for the hydrocracking of the pyrolysis fuel oil into the BTX fraction, *Catalysts* 10 (2020) 1152. DOI: 10.3390/catal10101152

[96]. E.A. Belopukhov, I.M. Kalashnikov, M.D. Smolikov, D.I. Kir'yanov, T.I. Gulyaeva, A.S. Belyi, Pt/BEA–Al2O3 catalysts for the isomerization of benzene/heptane mixtures. I: Optimizing the support's composition, *Catal. Ind.* 9 (2017) 48–53. DOI: 10.1134/S2070050417010032

[97]. N. Alimohammadi, S. Fathi, Selective benzene reduction from gasoline using catalytic hydrogenation reactions over zeolite Pd/13X, *React. Kinet. Mech. Catal*. 128 (2019) 949–964. DOI: 10.1007/s11144-019-01675

[98]. J.L. Rousset, L. Stievano, F.J.C.S. Aires, C. Geantet, A.J. Renouprez, M. Pellarin, Hydrogenation of toluene over γ-Al2O3-supported Pt, Pd, and Pd–Pt model catalysts obtained by laser vaporization of bulk metals, *J. Catal.* 197 (2001) 335–343. DOI: 10.1006/jcat.2000.3083

[99]. H. Liu, R. Fang, Z. Li, Y. Li, Solventless hydrogenation of benzene to cyclohexane over a heterogeneous Ru–Pt bimetallic catalyst, *Chem. Eng. Sci*. 122 (2015) 350–359. DOI: 10.1016/j.ces.2014.09.050

[100]. M. Sankar, N. Dimitratos, P.J. Miedziak, P.P. Wells, C.J. Kiely, G.J. Hutchings, Designing bimetallic catalysts for a green and sustainable future, *Chem. Soc. Rev*. 41 (2012) 8099–8139. DOI: 10.1039/C2CS35296F

[101]. A. Glotov, A. Vutolkina, A. Pimerzin, V. Nedolivko, G. Zasypalov, et al., Ruthenium catalysts templated on mesoporous MCM-41 type silica and natural clay nanotubes for hydrogenation of benzene to cyclohexane, *Catalysts* 10 (2020) 537. DOI: 10.3390/catal10050537

[102]. W. Wang, H. Liu, T. Wu, P. Zhang, G. Ding, et al., Ru catalyst supported on bentonite for partial hydrogenation of benzene to cyclohexene, *J. Mol. Catal. A: Chem.* 355 (2012) 174–179. DOI: 10.1016/j.molcata.2011.12.013

[103]. M.D. Argyle, C.H. Bartholomew, Heterogeneous catalyst deactivation and regeneration: A review, *Catalysts* 5 (2015) 145–269. DOI: 10.3390/catal5010145

[104]. N. Alimohammadi, S. Fatthi, Comparing the performance of heterogeneous Pd-supported catalysts: Pd/ZSM-5, Pd/13X and Pd/Al2O3 for the hydrogenation of benzene in a mixture of normal heptane and benzene, *Iran. J. Chem. Chem. Eng.* 18 (2021) 3–19. DOI: 10.22034/ijche.2022.318553.1418

[105]. C.H. Bartholomew, Mechanisms of catalyst deactivation, *Appl. Catal. A: Gen*. 212 (2001) 17–60. DOI: 10.1016/S0926-860X(00)00843-7

[106]. M.S. Hamdy, F.A. Alqahtani, M. Shkir, K.F. Fawy, M. Benaissa, et al., Effect of different zeolite supports on the catalytic behavior of platinum nanoparticles in cyclohexene hydrogenation reaction, *Catalysts* 12 (2022) 1106. DOI: 10.3390/catal12101106

[107]. K. Toshtay, A.B. Auezov, Hydrogenation of vegetable oils over a palladium catalyst supported on activated diatomite, *Catal. Ind.* 12 (2020) 7–15. DOI: 10.1134/S2070050420010109

[108]. M. Iwanow, T. Gärtner, V. Sieber, B. König, Activated carbon as catalyst support: Precursors, preparation, modification and characterization, *Beilstein J. Org. Chem*. 16 (2020) 1188–1202. DOI: 10.3762/bjoc.16.104

[109]. R.K. Kumar Mishra, B. Singh, B. Acharya, A comprehensive review on activated carbon from pyrolysis of lignocellulosic biomass: An application for energy and the environment, *Carbon Resour. Convers.* 7 (2024) 100228. DOI: 10.1016/j.crcon.2024.100228

[110]. M. Cattaneo, M. Stucchi, G.M. Veith, L. Prati, D. Wang, et al., Ru supported on micro and mesoporous carbons as catalysts for biomass-derived molecules hydrogenation, *Catal. Today* 357 (2020) 143–151. DOI: 10.1016/j.cattod.2019.05.009

[111]. M. Macino, A.J. Barnes, S.M. Althahban, R. Qu, E.K. Gibson, et al., Tuning of catalytic sites in Pt/TiO2 catalysts for the chemoselective hydrogenation of 3-nitrostyrene, *Nat. Catal.* 2 (2019) 873–881. DOI: 10.1038/s41929-019-0334-3

[112]. Y. Zhang, X. Yang, X. Yang, H. Duan, H. Qi, et al., uning reactivity of Fischer–Tropsch synthesis by regulating TiOx overlayer over Ru/TiO2 nanocatalysts, *Nat. Commun.* 11 (2020) 3185. DOI: 10.1038/s41467-020-17044-4

[113]. Z. Peng, X. Liu, S. Li, Z. Li, B. Li, et al., Heterophase-structured nanocrystals as superior supports for Ru-based catalysts in selective hydrogenation of benzene, *Sci. Rep.* 7 (2017) 39847. DOI: 10.1038/srep39847

[114]. D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, et al., Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, *Science* 279 (1998) 548–552. DOI: 10.1126/science.279.5350.548

[115]. A. Taguchi, F. Schüth, Ordered mesoporous materials in catalysis, *Micropor. Mesopor. Mat.* 77 (2005) 1–45. DOI: 10.1016/j.micromeso.2004.06.030

[116].K. Toshtay, A.B. Auyezov, Zh.A. Bizhanov, A.T. Yeraliyeva, S.K. Toktasinov, et al., Effect of catalyst preparation on the selective hydrogenation of vegetable oil over low percentage Pd/diatomite catalysts, *Eurasian Chem.-Technol. J.* 17 (2015) 33–39. DOI: 10.18321/ectj192

[117].K. Toshtay, A. Auyezov, Y.A. Aubakirov, R. Amrousse, S. Azat, et al., Palladium–nickel supported and palladated activated diatomite as an efficient catalyst for poly-α-olefins hydrogenation, *Catal. Surv. Asia* 27 (2023) 296–305. DOI: 10.1007/s10563-023-09394-y

[118].K. Toshtay, Liquid-phase hydrogenation of sunflower oil over platinum and nickel catalysts: Effects on activity and stereoselectivity, *Results Eng.* 21 (2024) 101970. DOI: 10.1016/j.rineng.2024.101970

[119].R.K. Widi, D.C. Trisulo, A. Budhyantoro, R. Chrisnasari, Preparation of immobilized glucose oxidase wafer enzyme on calcium-bentonite modified by surfactant, *IOP Conference Series: Materials Science and Engineering* 223 (2017) 012050. DOI: 10.1088/1757-899X/223/1/012050

[120].Y. Jia, W. Han, G. Xiong, W. Yang, Diatomite as high performance and environmental friendly catalysts for phenol hydroxylation with H2O2, *Sci. Technol. Adv. Mater.* 8 (2007) 106–109. DOI: 10.1016/j.stam.2006.10.010

[121].E.E. Doğan, P. Tokcan, B.K. Kizilduman, Storage of hydrogen in activated carbons and carbon nanotubes, *Adv. Mater. Sci.* 18 (2018) 5–16. DOI: 10.1515/adms-2017-0045

[122].P.D. Svensson, The Bentonite Barrier: Swelling Properties, Redox Chemistry and Mineral Evolution, Lund University, Lund, 2015, p. 81.

[123].N. Wilkinson, A. Metaxas, C. Quinney, S. Wickramaratne, T.M. Reineke, C.S. Dutcher, pH dependence of bentonite aggregate size and morphology on polymer-clay flocculation, *Colloids Surf. A: Physicochem. Eng. Asp.* 537 (2018) 281–286. DOI: 10.1016/j.colsurfa.2017.10.007

[124].G. Zhou, J. Liu, X. Tan, Y. Pei, M. Qiao, et al., Effect of support acidity on liquid-phase hydrogenation of benzene to cyclohexene over Ru–B/ZrO2 catalysts, *Ind. Eng. Chem. Res*. 51 (2012) 12205–12219. DOI: 10.1021/ie301302x

[125].A.A. Reka, B. Pavlovski, E. Fazlija, A. Berisha, M. Pacarizi, et al., Diatomaceous earth: Characterization, thermal modification, and application, *Open Chem*. 19 (2021) 451–461. DOI: 10.1515/chem-2020-0049

[126].Patent CN102219633A, Publ., (2013), Method for preparing cyclohexane through benzene hydrogenation by concerted catalysis of normal pressure plasma.

[127].N.S. Mussa, K. Toshtay, F. Dumeignil, Recent developments in the field of MOF-based catalytic systems: A review, *Appl. Catal. A: Gen.* 708 (2025) 120555. DOI: 10.1016/j.apcata.2025.120555

[128].C.-F. Du, X. Zhao, Z. Wang, H. Yu, Q. Ye, Recent advanced on the MXene–organic hybrids: Design, synthesis, and their applications, *Nanomaterials* 11 (2021) 166. DOI: 10.3390/nano11010166

[129].X.-H. Tan, G.-B. Zhang, R.-F. Du, Y. Pan, K.-N. Fan, et al., Partial hydrogenation of benzene to cyclohexene over novel Ru-B/MOF catalysts, *Acta Phys.-Chim. Sin*. 30 (2014) 932–942. DOI: 10.3866/PKU.WHXB201403212

[130].N.S. Mussa, K. Askaruly, K. Bexeitova, S. Azat, K. Toshtay, Recent advancements in MXene-based catalysts: Synthesis, characterization, and applications in sustainable energy production, *Carbon Trends* 20 (2025) 100551. DOI: 10.1016/j.cartre.2025.100551

[131].N.S. Mussa, S. Azat, K. Toshtay, Catalytic applications of MXene-based materials and their derivatives, *ACS Omega* 11 (2026) 18525–18546. DOI: 10.1021/acsomega.5c11762

[132].R. Shi, X. Wang, G. Zhou, Electronic metal–support interaction directed electron-deficient nanoparticulate Ru on Ti3C2 MXene-derived TiO2 nanoflowers for robust benzene semi-hydrogenation, *Appl. Surf. Sci.* 624 (2023) 157159. DOI: 10.1016/j.apsusc.2023.157159

[133].M. López, Á. Morales-García, F. Viñes, F. Illas, Thermodynamics and kinetics of molecular hydrogen adsorption and dissociation on MXenes: Relevance to heterogeneously catalyzed hydrogenation reactions, *ACS Catal*. 11 (2021) 12850–12857. DOI: 10.1021/acscatal.1c03150