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Advances in Catalytic Isomerization Using Heteropolyacid-Based Nanocomposites: A Comprehensive Review

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Abstract

Catalytic isomerization is a process used to increase the octane number of light naphtha fraction and thus aids in extending the life of automobile engines. Researchers are still working to prepare more effective and less expensive isomerization catalysts to replace the costly previous catalysts. Ongoing challenges in this field seek to design highly active isomerization catalysts operated under moderate conditions while keeping high branched-isomer selectivity. Heteropolyacids (HPA) have been presented as the most capable substitutes to fulfill the requirements. They are considered bifunctional catalysts that perform dehydrogenation /isomerization followed by hydrogenation because of their firm acidity and redox properties. Some catalytic-isomerization studies were started utilizing HPA in combination with platinum, which significantly improves the selectivity and stability. Thus, HPA-based bifunctional catalysts can provide enough acid and hydrogenation–dehydrogenation sites sufficiently. However, the most ongoing challenge in this field is the poor thermal stability of HPAs, which limits their use at higher temperatures for vapour-phase reactions. This review aims to highlight the recent progress in catalytic isomerization of alkanes using heteropolyacids supported on different carriers, with and without noble metals.

Keywords: Catalytic Isomerization, Alkanes, Keggin, Heteropolyacids, Supported.

التقدم الحالي في الأيزومرية الحفزية على المركبات النانوية القائمة على الأحماض غير المتجانسة كمحفزات غير متجانسة

علاء جاسم عوض، سعد حنش عمار

الخلاصة:

الأيزومرية الحفزية هي عملية تستخدم لزيادة رقم الأوكتان لجزء من النافتا الخفيفة وبالتالي تساعد في إطالة عمر محركات السيارات. ولا يزال الباحثون يعملون على إعداد محفزات متماكبة أكثر فعالية وأقل تكلفة لتحل محل المحفزات السابقة المكلفة. تم تقديم الأحماض المتغايرة (HPA) باعتبارها البدائل الأكثر قدرة على تلبية المتطلبات. وهي تعتبر محفزات ثنائية الوظيفة تؤدي عملية نزع الهيدروجين/الأيزومرة تليها الهدرجة بسبب حموضتها الثابتة وخصائص الأكسدة والاختزال. تهدف هذه المراجعة إلى تسليط الضوء على التقدم الذي تم إحرازه مؤخرًا في الأيزومرة الحفزية للألكانات باستخدام الأحماض المتعددة غير المتجانسة المدعومة على ناقلات مختلفة، مع أو بدون معادن نبيلة.

1. Introduction

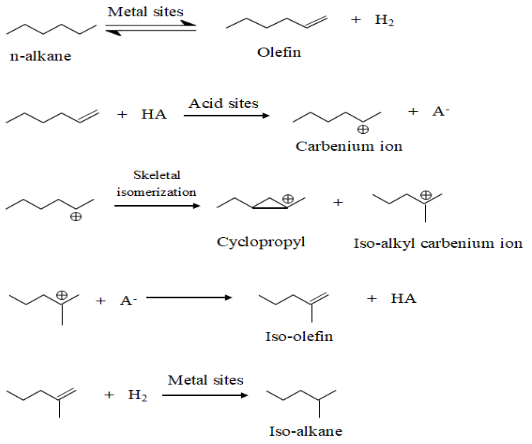
The focus of the petroleum industry is virtually exclusively on catalysis. The primary explanation for this phenomenon is that in petrochemical synthesis, catalytic routes are superior to direct thermal reactions in their ability to control the product's selectivity. Because of the growing demand for petrol and the anticipated future shortages of crude oil, the businesses that produce refined products have been compelled to develop new procedures and ways for extracting the most value possible from the oil. These alkanes are widely distributed in crude oil and are normally transformed into more useful compounds by means of isomerization. [1]. Production of cleaner and more efficient fuels depends critically on the development of extremely active catalysts for the isomerization of n-alkanes, such regular hexane. Reducing dependence on regulated and environmentally problematic additives like aromatics and olefins can also be a benefit of the process of turning n-alkanes into isomers. A challenge is to provide effective and reasonably priced catalytic materials for isomerization procedures in the petroleum refining sector.[2]. of interest in

In the world of petroleum refining, the catalytic isomerization of ordinary hexane to make high octane gasoline is very interesting. As it converts low-octane n-paraffins into higher octane iso-paraffins, isothermization is an essential process in the synthesis of high-octane gasoline. But the emissions produced by car combustion processes damage the environment and enable the additives to escape into the atmosphere. The rising market for high-octane gasoline and the need for catalysts that can perform two functions in the naphtha reforming process are the two main causes of the growing interest in isomerization technologies. These elements have to be taken into account in view of the necessity to protect the ecology. Thus, a vital and fundamental part of the petroleum industry has become the catalytic synthesis of branched-chain hydrocarbons from straight-chain hydrocarbons [29–31].

Early in the 18th century, Berzelius first the idea of isomerization to the discipline of organic chemistry; Markovnikov took the process even further in 1865. Acids may accelerate the isomerization of n-alkanes to branched alkanes, as Markovnikov found. The development of the catalytic isomerization of n-alkanes to branched alkanes was made possible by this finding. One crucial process in the petrochemical sector is the isomerization of n-alkanes to branched alkanes. Low octane number straight-chain alkanes are converted into higher octane number branched-chain alkanes using it. We call this phenomena hydroisomerization. The changing of the atomic bond arrangements inside molecules is the hallmark of isomerization, a chemical change. Maintaining the chemical formula, such a modification makes it easier for molecules to go from a linear to a branching structure. Stems are changed from linear alkanes to branched alkanes while keeping the same number of carbon atoms. There is also a simultaneous transformation of cycloalkanes into naphthenes, which have a greater degree of branching. Isomers are a type of chemical variant that has the same molecular formula but different structural formulae. These chemical variants are known as isomers[5][6]. Isomerization processes are influenced by several parameters, including temperature, flow rate, pressure, the molar ratio of hydrogen to hydrocarbon, the efficiency of the catalyst, the composition of the substrate, and the presence of impurities. [7]. In order to transform straight-chain alkanes into their branched isomers, it is important to employ a catalyst that exhibits exceptional efficiency and functions at the optimal temperature. On bifunctional metal-acid catalysts, n-alkanes can undergo isomerization through the catalytic process. The process begins with alkane dehydrogenation at metal sites, followed by the isomerization of the resulting olefin at acid sites through a mechanism known as carbocation (carbonium ion). Subsequently, the formation of iso-olefins leads to the production of branched alkanes through the hydrogenation of the iso-olefins at metal sites. Platinum is commonly used as the metal phase in bifunctional isomerization catalysts, while acidic supports, such as chlorinated alumina, sulfated zirconia, and zeolite, are often utilized for the acid component. To minimize the production of coke from this process, hydrogen is usually added to the feed. The isomerization of n-hexane to 2-methylpentane occurs through a sequence of reactions. The initial stage involves the dehydrogenation process of n-hexane, resulting in the formation of hexene. Subsequently, hexene undergoes isomerization to produce 2-hexene. The last stage is the hydrogenation of 2-hexene to produce 2-methylpentane.[8]

Without the presence of metallic substances, the conversion of alkanes can also be accelerated by using strong acid catalysts, namely single-function acid catalysts. This process begins with the commencement of a chain reaction to generate active carbocation intermediates. These intermediates then undergo rearrangement as part of the chain propagation phase, ultimately leading to chain termination. A wide range of solid acids, such as zeolites, sulfated zirconia, and heteropolyacids, can effectively assist the conversion of linear alkanes into their branched isomers. Cracking and alkylation are two potential inadvertent consequences that might arise from this technique [9]. The first stage in the process of creating liquid superacids involves removing the hydrogen from the alkane molecule. Without an acid with a strong enough pH value, the isomerization process does not occur [9-10]. The skeletal isomerization of carbonium ions is the second phase in the cycle, and it takes place as a result of a rearrangement of the protonated cyclopropane (PCP). Through the PCP intermediate, rearrangement is only possible with n-alkanes with a longer chain than the C4 chain. In the phase of chain propagation, rearranged carbonium ions may potentially extract an H- from an alkane, resulting in the formation of an isoalkane and a new carbonium ion. [9].

The catalytic isomerization of alkanes over a dual functional metal-acid catalyst (Scheme 1) occurs firstly by alkane dehydrogenation over metal sites, forming olefin intermediates [11]. The formed olefins are protonated on the acid sites, forming carbonium ions. Then, carbonium ions undergo skeletal isomerization to form iso-alkyl carbonium ions through cyclopropyl cation. Then, the iso-alkyl carbonium ions are converted to iso-olefin intermediates by proton removal. Finally, the iso-olefin is hydrogenated over metal sites to generate iso-alkane.



Scheme (1): Catalytic isomerization of n-alkane over duel functional metal-acid ecatalyst.

The crucial aspect of isomerization catalyst development is to select the appropriate acid part.

Strong acidity is present in bulk heteropolyacids (HPAs) and their salts. HPAs are a class of inorganic compounds that are composed of transition metal cations (for instance, tungsten, molybdenum, and vanadium) and oxygen, with the addition of non-metallic atoms such as phosphorus, silicon, and arsenic. HPAs are complex anionic types with unique chemical and physical features, including high acidity, redox reactivity, and catalytic and photocatalytic activities. HPAs are typically produced by reacting metal oxides or salts with acid or their anions. The most frequently considered HPAs contain tungsten and molybdenum, like the Keggin type of phosphotungstic acid ($H_3PW_{12}O_{40}$) and phosphomolybdic acid ($H_3PMo_{12}O_{40}$). Accordingly, HPAs have established applications in multiple exciting fields, including catalysis, electrochemistry, and material science. They are used as solid acid catalysts in organic reactions such as esterification, alkylation, and oxidation and as photoactive semiconductor-like in photocatalysis and photocatalytic fuel cells.

2. Alkane Isomerization

Is a complicated mechanism in which new carbon-carbon bonds are formed as well as existing ones are broken. The process progresses by hydrogenation, dehydrogenation, isomerization, and cracking. High-octane gasoline is produced in industrial settings by isomerization of the difficult-to-decompose stable C5-C6 linear alkanes. By converting n-hexane to 2-methylpentane (2MP) and 3-methylpentane (3MP), the research octane number (RON) is raised from 25 to 74. The addition of branching into the molecules increases the RON even more, producing 2,2- and 2,3-dimethylbutane isomers (22DMB and 23DMB) with RON values of 100 and 98. [1].

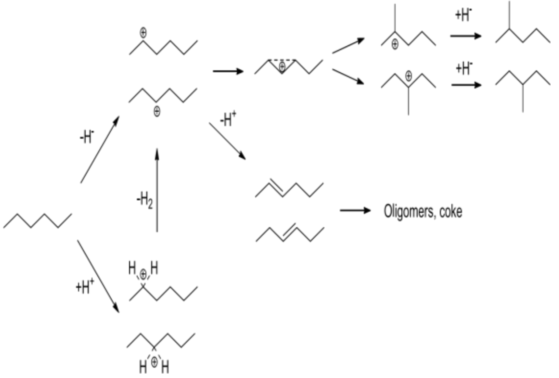


Figure (1): Acid-catalyzed monomolecular mechanism for catalytic isomerization of n-C_6 [2]

An acid-catalyzed route on strong Lewis and Bronsted acid sites [2] (Fig. 1). is required for the alkane isomerization reaction to take place (see Fig. 1). Within the context of Lewis acid-catalyzed reactions, linear alkanes such as n-hexane can be subject to isomerization through a unimolecular carbonium-ion chain mechanism. The synthesis of carbonium ions, precipitated by the abstraction of a hydrogen atom at the active sites offered by Lewis acids, starts this complex process. The carbonium ions then participate in the protonation of an intermediate cyclopropane. After that, this intermediate migrates a methyl group, and then another n-hexane molecule transfers a hydrogen.

Such a sequential progression yields the primary isomerization products, mono-branched 2-methylpentane (2MP) and 3-methylpentane (3MP), alongside the regeneration of carbonium ions that perpetuate the chain mechanism. The production of 23DMB and 22DMB can occur due to subsequent isomerization of 2MP and 3MP. The protonation of a C-H bond results in the formation of carbonium ions at places with a strong Bronsted acid. The carbonium ions are subject to an elimination process of hydrogen molecules, leading to the formation of carbonium ions, which in turn give rise to 2-methylpropane (2MP) and 3-methylpropane (3MP). The abstraction of a proton from these carbonium ions can facilitate the synthesis of alkenes. These alkenes are capable of undergoing oligomerization and forming coke, both processes contributing to the catalytic deactivation (as illustrated in Figure 1). Moreover, the breakdown of hexane isomers might result in the production of hydrocarbons of the C6 variety. The merging of C6 carbonium ions and an alkene through a bimolecular process can lead to the formation of C12 cation intermediates. These intermediates can undergo disproportionation, resulting in the production of both C6 compounds and compounds with more than six carbons (C6+ compounds). The presence of C6+ compounds has the potential to result in the development of coke, which can have a detrimental effect on the effectiveness of the catalyst. [2].

The commercial isomerization of linear alkanes can be achieved by using bifunctional metal-acid catalysts, such as Platinum supported on chlorinated alumina substrates or acidic zeolites like mordenite, in the presence of hydrogen (hydrodimerization). [1]. Based on Fig. 2, the reaction will first include the dehydrogenation of alkanes on platinum sites. Then, it will continue with the isomerization of alkenes generated on the acid sites of the support. After this step, the alkene isomer is subjected to hydrogenation on the Platinum, forming the branched alkane. The acid-catalyzed process (Fig. 1) is significantly less effective than its counterpart, the bifunctional system (Fig. 2). Platinum, as a component of the bifunctional catalyst, plays an essential role not only in speeding up the process of isomerization but also in lowering the amount of alkene present in the steady state. The latter improves reaction selectivity by decreasing the involvement of the bimolecular process[14], which minimizes coke generation, enhancing the catalyst's lifespan [1].

In order to create catalysts that may perform various tasks, it is necessary to combine one or more precious metals with a substrate. The choice of whether the substrate is acidic or basic depends on the specific reaction desired. Nevertheless, a notable obstacle exists in preserving the reactivity of the catalytic sites under different reaction circumstances for an extended period. This characteristic is especially critical for isomerization processes, where the catalyst needs to endure high temperatures and prevent deactivation[15].

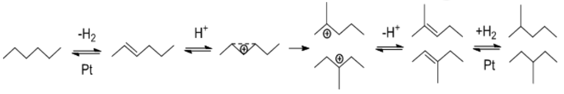
The process involves three basic steps [16][17]. First, n-alkane is converted to a corresponding alkene through dehydrogenation on the metal surface. Second, the generated alkene undergoes attachment at the sites of Brønsted acids, culminating in the production of a carbonium ion during the intermediary state. After then, this ion undergoes isomerization and is released. This causes the first alkene to hydrogenate on the metallic surface, therefore producing the first alkane. Remarkably, the crucial rate-determining step of the reaction turns out to be the hydrogenation phase of the first alkene.

3. Heteropolyacids (HPAs)

3.1 Introduction

Heteropolyacids (HPAs) are a class of solid acids that exhibit promise as catalysts for a wide range of processes. HPAs have remarkable efficiency in facilitating the transformation of linear alkanes into branched alkanes, owing to their extraordinary acidity and heat stability. HPAs have shown notable effectiveness and selectivity in the conversion of linear alkanes into branched alkanes by isomerization. HPAs have remarkable effectiveness in the conversion of n-alkanes into branched alkanes, mostly because to their high acidity and thermal stability. HPAs have shown notable effectiveness and selectivity in the conversion of linear alkanes into branched alkanes by isomerization. HPAs, also known as heteropolyacids, are solid acids that show promise as catalysts for several processes. HPAs have remarkable effectiveness in converting n-alkanes into branched alkanes due to their high acidity and thermal stability[12][24]. In recent times, scientists have conducted thorough investigations on combined Pt-HPA bifunctional catalysis for catalytic isomerization of alkane. These studies have shown that this procedure is highly successful[6–9].

Heteropolyacids (HPAs) are a class of Bronsted acids defined by specific metal and non-metal oxygen-containing polyoxometalate (POM) anions. When $x \leq m$, the usual formula for polyoxometalate anions is [XxMmOy]n-, where X stands for heteroatoms such as Ge4+, Si4+, B3+, P5+, and As5+ and M for addenda metal ions such Mo (VI), W (VI), Nb(V), Ta(V), and V (V), or their combinations. Wide range of HPAs with different structures and functions are produced by the variety of combinations of X and M. [24]. The discovery of the first heteropolyacid dates back to 1826 by Berzelius. Since then, numerous heteropoly compounds have been synthesized and their structures have been determined. In 1934, the use of X-ray diffraction techniques by Keggin resulted in the discovery of the structure of a significant type of heteropoly acid (HPA), which was later named after him. Further structural variants, such as those named after Wells-Dawson, Dexter-Silverton, Anderson-Evans, Lindqvist, and others, have been delineated. The architecture of the Keggin structure is characterized by a spherical arrangement constituted by 12 MoO6 octahedra, with phosphorus occupying the central position [25][19]. Fig. 3 shows some PMO structures.



Figure(2): Bifunctional catalyzed pathway for n-hexane hydroisomerization.

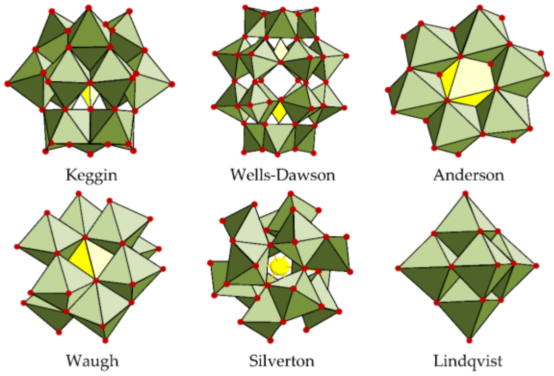
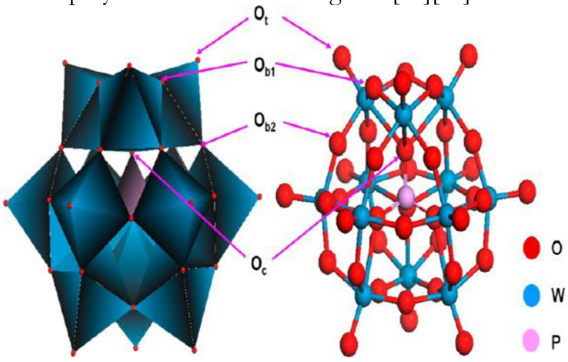


Figure (3): Polyhedral illustration of some POMs assemblies (Copyrights 2015, Springer)[26].

Because of their high Bronsted acidity, heteropoly acids have found usage in a wide variety of applications, most notably in the field of catalysis. Acids classified as HPAs are more potent than traditional acids such as zeolites and metal oxides. Are HPAs very acidic and possess unique structural mobility and multifunctionality, both of which have led to an explosion in the number of uses for these compounds. [24]. The Keggin-type HPAs are the most stable, available, and commonly used for catalysis heteropolyacids. The Keggin type inions are represented by the formula $[XM_{12}O_{40}]^{8-n}$, where X is the central atom (commonly Si^{4+}, P^{5+}, etc.), x is its oxidation state, and M is the metal ion (such as W^{6+} and Mo^{6+}). The structure of the Keggin $PW_{12}O_{40}^{3-}$ heteropoly anion is shown in Fig. 4.1 [27][28].



Figure(4): The structure of Keggin $PW_{12}O_{40}^{-3}$ inion (Copyrights 2014, ACS publications)

3.2. Catalytic properties of HPAs

HPAs have long attracted researchers' attention due to their distinctive characteristics, and they have been utilized in various fields, including pharmaceuticals, materials, catalysis, and photocatalysis. The exceptional qualities of HPAs make them particularly interesting for use in catalysis, such as their ability to adjust acidity and redox properties, resist oxidative decomposition, and good thermal stability. These remarkable features are closely linked to its structures and compositions, which offer a diverse range of compositions required to evaluate the effects of composition on catalytic reactivity.

3.2.1 Active acid sites of HPAs

HPAs exhibit adaptability as catalysts owing to their several active sites, including metals, protons, and oxygen atoms. HPAs and their salts exhibit significantly stronger Bronsted acidity compared to traditional acid catalysts such zeolites and oxides, which enhances acid-catalyzed reactions. The presence of proton sites in HPA is responsible for its extreme acidity. The acidity of the HPA is mostly derived from proton (Bronsted) and Lewis acid sites. These proton sites are produced by salt reduction and partial hydrolysis of poly anions. [29][30]. In HPAs, proton sites come in two varieties: hydrate and nonahydrate proton types, as Fig. 5 illustrates. [24]. The mobility of hydrated protons is very high, and they are the leading cause of the high proton conductivity of HPA hydrates. On the other hand, the protons in the nonahydrate type are firmly fixed to the oxygen atoms at the edges of the poly anion.

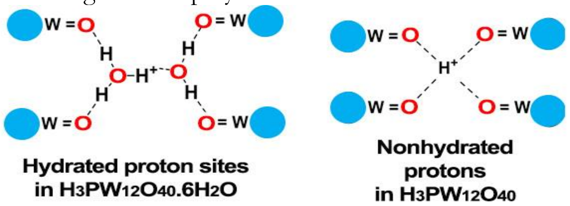


Figure (5): Representation of structures of hydrate and nonahydrate proton types in $H_3PW_{12}O_{40}$

The proton sites on the HPA surface play a significant role in their effectiveness as catalysts with heterogeneous acid properties. Typically, crystalline HPAs have a very small surface area, ranging from 1-5 m2/g, and thus low porosity. To increase their surface area, they can be supported or immobilized on a high surface support like alumina and carbon, which helps to expose the proton sites. [21],[29],[31]. The acidity levels in Heteropoly Acids (HPAs) may be properly measured using thermal desorption methods using alkaline agents like ammonia and pyridine. Izumi and colleagues conducted a study where they used temperature-programmed desorption (TPD) with ammonia to evaluate the acidic properties of several Keggin HPAs. They found that H3PW12O40, H4SiW12O40, H3PMo12O40, and H4SiMo12O40 had NH3-desorption temperatures of 592°C, 532°C, 463°C, and 423°C, respectively. Additionally, it has been elucidated that the acidity of HPAs is contingent on the identity of the metal atoms incorporated within the structure, as well as the valence states of the metals [32].

3.3. Thermal stability

HPAs are widely utilized as heterogeneous catalysts due to their important feature of thermal stability. These compounds can endure moderately high temperatures up to 300-350 °C and remain thermally stable. However, during the catalyst regeneration process to remove cokes, using HPAs can be problematic as it requires high-temperature treatment, typically around 500 °C [19]. The thermal decomposition temperature is used to measure thermal stability, where all acid sites are released with increasing temperature, as shown in Fig. 6 [21]. Usually, the Keggin types have higher thermal stability than other HPAs. The decomposition temperature, which was tested by TGA analysis, of $H_3PW_{12}O_{40}$ may reach 485 C.

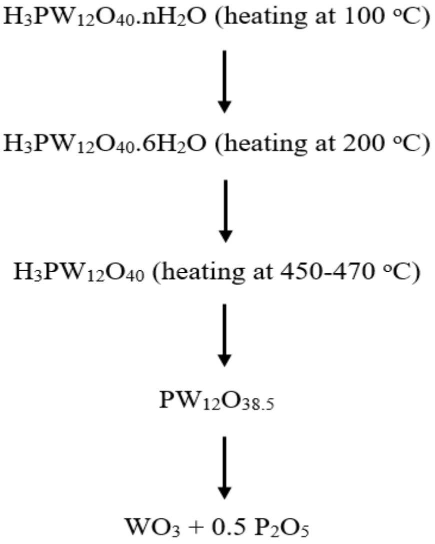


Figure (6): Thermal decomposition of hydrous $H_3PW_{12}O_{40}$

4. HPAs as multifunctional isomerization catalysts

The basic in developing the catalytic isomerization process is selecting the catalyst part that provides the appropriate acidity. HPAs and their salts provide high acidity and are commonly used as multifunctional catalysts in this field. Phosphotungstic hetero-polyacid ($H_3PW_{12}O_{40}$) is the most vital type of HPA and is frequently utilized in catalytic isomerization requests [19]. In a study by Misono et al., the effectiveness of Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as an isomerization catalyst for n-pentane was investigated [33].

According to Essayem et al., under specific circumstances, the activity and selectivity of the Pt-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst system were significantly better than those of Pt supported on H-ZSM-5 [34]. According to Okuhara et al. [18], n-alkanes isomerization can be achieved by $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ HPA salt with high acidity and good surface area, coupled with noble metals as multifunctional catalysts. Numerous researchers adopted the supported HPA and noble metals multifunctional isomerization catalysts. Silica, zirconia, zeolites, and alumina have been widely applied as high-surface supports.

Sun et al. [35] synthesized platinum as an active component supported on 40%HPMo (phosphomolybdic acid)-MCM-41 as a mesoporous and high surface area support. They achieved a high jet fuel yield (≈ 20 wt%). Moreover, MCM-41 was also used as a support by Chen et al. after modification by Zr and deposition with phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW) and Platinum. They stated that the fabricated Pt(1wt%)/HPW(25wt%)/Zr-MCM-41 catalysts showed high performance for hydroisomerization of n-C_6, reaching 100% selectivity (i-C_6%) at reaction temperatures of 260 °C. They also stated that increasing Zr content in MCM-41 support leads to higher n-C6 conversions, lowering the i-C_6 selectivity [36]. Table 1 summarizes the related previous studies.

Recently, metal-organic frameworks (MOFs) were used to support the catalytic isomerization process. Rezaei N. and Taghizadeh M. et al. prepared a Zr-metal-organic framework (UiO-66) as support material. They deposited Pd and Pt noble metals and hetero-poly phosphomolybdic acid (HPMo) onto UiO-66. The Pd-Pt/HPMo/UiO-66 catalyst system showed iC_6 selectivity of 86% and n-hexane conversion of 72.1% after 36 h at 180 C [37]. The authors of another work used highly porous MIL-101 MOFs as supporting material [38]. They achieved 92.5% iC_6 selectivity and 75.3% nC_6 total conversion over (Pd+Pt)/HPMo/MIL-101 at 180 C reaction temperature. Wei et al. prepared 0.4% Pt supported on MIL-101(Cr) acidified by HSiW (silicotungstic acid) as bifunctional isomerization catalysts. According to their work, the catalytic activity of Pt/HSiW/MIL-101(Cr) was meaningfully enhanced, reaching 58.93% n-heptane conversion and 95.68% iso-heptane selectivity, at specific conditions (reaction time = 2 h and temperature = 260 °C) [39].

Table (1): HPA-based nanocomposites as heterogeneous catalysts for the isomerization process.

Catalyst system	Reaction type/conductions	Results	Ref.
Pt/CsPW Pt-Au/CsPW (bimetallic)	n-hexane Isomerization. 180–220 °C, atmospheric pressure, n-hexane to H_2 partial pressures (P_{C6}/P_{H2}) of 0.06–0.24.	Average conversion over 5.57%Pt-4.25%Au/CsPW catalysts = 10.7 after 6 h time on stream	[40]
$H_3PW_{12}O_{40}$/MCM-41	Esterification of acetic acid with n-octanol		[41]
Pt/40 wt% HPMo/MCM-41	hydrocracking and isomerization of n-C_{16} to jet fuel	The highest yield of jet fuel ≈ 20 wt% was obtained over Pt/40 wt.% HPMo/MCM-41 (WHSV=1 h^{-1})	[35]
Pd + $H_3PW_{12}O_{40}/SiO_2$	n-hexane Isomerization		
$H_3PW_{12}O_{40}$/Y-zeolite	n-hexane Isomerization		[42]
HPW/SBA-15	n-hexane Isomerization. Gas-phase isomerization of n-hexane at 200 °C.	Conversion = 22.5% at 0 min, 7.6% at 12 h. Selectivity (iC6%) = 84.5%	[43]
HSiW/SBA-15		Conversion = 20.7% at 0 min, 7.5% at 12 h. Selectivity (iC6%) = 89.7%	
Keggin HPW and HPW11Zr, Dawson HP2W18 and HP2W21 supported on zirconia	n-hexane Isomerization.	iC6 yield = 80% selectivity= 96–98% at 190 °C.	[22]
Pt/$H_3PW_{12}O_{40}$/Zr-MCM-41	n-hexane hydroisomerization	Selectivity to iC_6= 100% at below 260 °C.	[36]
Pt/CsPW, Au/CsPW and PtAu/CsPW	Isomerization of cyclohexane. Reaction temperature = 180-300 C, normal pressure, and a cyclohexane/H_2 partial pressure = 0.04-0.14.	selectivity to methyl cyclopentane = >99%	[44]
HSiW/Pt/SBA-15	Isomerization of n-hexane	selectivity to iC_6 = 98% conversion = 55%	[45]
Pt-$H_3PW_{12}O_{40}$/SBA-15	Isomerization of n-hexane	Global conversion = 66.5% selectivity to iC_6 = 96.4%	[46]
Pd+Pt/HPMo/UiO-66	Isomerization of n-hexane. Temperature = 180 °C, WHSV= 3 h^{-1}, and H_2/n-C_6 = 2	iC6 selectivity = 86% n-hexane conversion = 72.1% after 36 h.	[37]
(Pd + Pt)/HPMo/MIL-101	n-hexane hydroisomerization. temperature =180 °C, H_2/nC_6 molar ratio = 2, and WHSV = 3 h^{-1}	92.5% iC_6 selectivity 75.3% nC_6 conversion	[38]
Pt/$H_3PW_{12}O_{40}$/SBA-15	n-heptane hydroisomerization	Pt(1wt%)/$H_3PW_{12}O_{40}$(20wt%)/SBA-15 catalyst provides 100% selectivity and 56.74% n-heptane conversion at 320 °C temperature.	[47]
Pt/HSiW/KIT-6	n-butane isomerization.	n-butane conversion = 72% isobutane yield = 56.8%	[48]

	temperature = 250 °C, WHSV = 0.15 h–1, at the beginning of the reaction		
Pt-$H_4SiW_{12}O_{40}/SiO_2$ and Pt-$H_3PW_{12}O_{40}/SiO_2$	n-butane isomerization.	High stability and high selectivity (> 97%) to iso-butane.	[49]

5. Conclusions and future outlooks

This paper provides a comprehensive overview of HPAs-based composites that have gained interest as potential isomerization catalysts due to their suitable acidity, moderate stability, and low cost. HPAs materials show promising catalytic properties in several important applications, including catalytic isomerization of naphtha fuel, due to their highly acidic properties, thus enhancing conversion and selectivity.

Phosphotungstic ($H_3PW_{12}O_{40}$) and silicotungstic ($H_4SiW_{12}O_{40}$) heteropolyacids are the most vital types of HPAs commonly utilized in catalytic isomerization requests. It can be used alone or with noble metals such as platinum and palladium, which improves the selectivity toward isomers and stability. It can also be loaded onto a supporting material with a high surface area, such as alumina, zeolites, and zirconia. Due to the high acidity and the good stability provided by HPAs, it became possible to dispense with the commercial chlorined Pt/Al_2O_3 catalyst. Also, many previous studies focused on searching for suitable acidity and surface area supports. Among these studies, niobium oxide is not a supporting material for HPAs, the noble metal, or both. Therefore, niobium oxide can be adopted as a new material.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution

Alaa J. Awadh: Writing – original draft.

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