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Catalytic Isomerization of Olefins and Their Derivatives: A Brief Overview

Wangjing Ma, Bonan Liu, Duanda Wang, Jun Zhao, Lu Zhang and Lei Zhang

Abstract

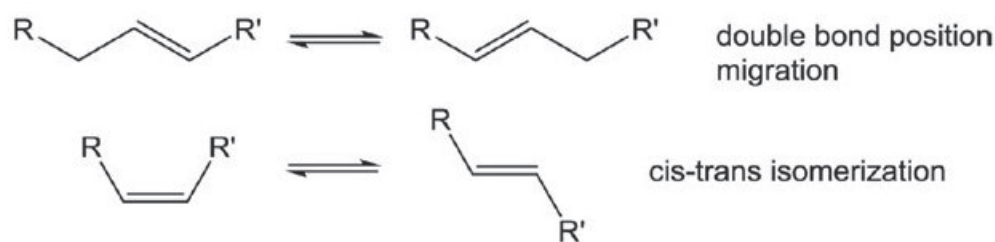
Carbon–carbon double bond (CCDB) isomerization is a method for synthesizing new organic compounds from olefins and their derivatives, which was based on C=C migration along carbon chain and cis/trans transform, and it plays a vital role in the fields of organic synthesis, synthesis of daily chemicals, raw oil's development and synthesis of natural products and so on. In this paper, advances of five types of catalytic methods for CCDB of olefins and their derivatives since the 1960s were discussed in detail; Based on his recent work, the author mainly introduces the application and development of photocatalysis in CCDB of olefins and their derivatives.

Keywords: olefins, carbon–carbon double bond, isomerization, photocatalyst

1. Introduction

Olefins, also known as alkenes, are examples of unsaturated hydrocarbons and are made up of hydrogen and carbon atoms only and contain one or more pairs of carbon–carbon double bonds (CCDB). One CCDB consists of one sigma bond and one pi bond and is stronger than carbon–carbon single bond ($611 \text{ kJ}\cdot\text{mol}^{-1}$ for C=C vs. $347 \text{ kJ}\cdot\text{mol}^{-1}$ for C-C), shorter than carbon–carbon single bond (average bond length: 0.134 nm for C=C vs. 0.154 nm for C-C). Depending on the position of the CCDB, olefins can be divided into terminal olefins, that the double bond is located at the terminal of a linear carbon chain (also called α -alkenes), and internal olefins, that the double bond is taking place at the inner side of carbon chain. It was valuable to study the effects of a CCDB's migration along the carbon chain on the hydrocarbons' activity and applications of a CCDB's migration along the carbon chain in oil drilling, surfactants, lubricants, fine chemicals, agrochemicals, pharmaceuticals, and other fields.

The following discussion will focus mainly on the isomerization of olefin, or migration of CCDB on linear alkenes. The functionalities of olefins, mainly for industrial and pharmaceutical purposes, vary by the location of CCDB on the alkene chains herein. Migration of CCDB is an important atom-economic reaction. New high valuable alkenes can be obtained from some inexpensive ones using the CCDB's migration along the carbon chain or cis/trans isomerism, as shown in **Figure 1**.

**Figure 1.**

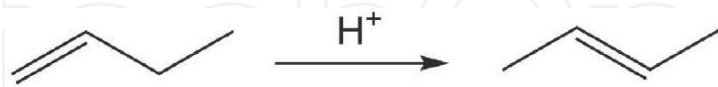
C=C isomerization of alkenes. R, or R' = -H, -OH, alkyl, alkenyl, phenyl, cycloalkyl, cycloalkenyl, -CHO, -COOH, -COOR etc.

It is difficult for alkenes to synthesize positional or geometrical isomer by the conventional method, while relatively easier by isomerization [1]. In general, there are five methods to realize the olefine isomerization: acid catalysis, basic catalysis, molecular sieves, organometallic chain-walking catalysis, photocatalysis. These catalysis function mechanism varies, has the characteristic respectively. In the rest of the chapters, these five major categories of olefin isomerization methods will be explained in detail.

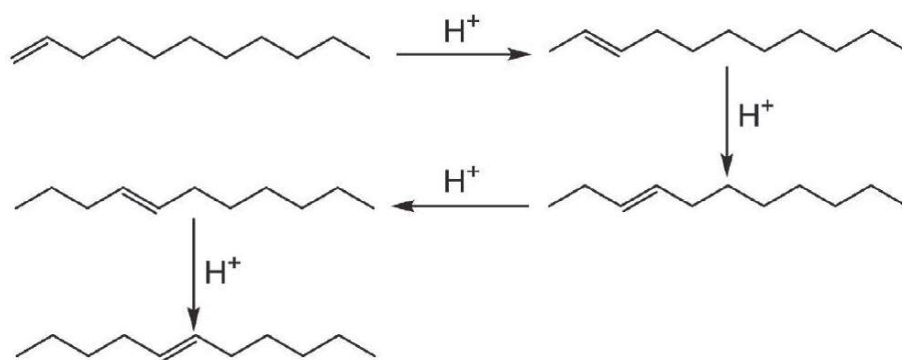
2. Acidic catalysis

The terminal linear alkenes generally range of C4 through C20 were isomerized to internal linear alkenes over a selective, strong acid catalyst to improve the positive CCDB isomerization and not catalyze oligomerization, cracking, skeletal isomerization, or alkylation. Firstly, the interaction of CCDB and acidic catalyst creates dissociation proton and then active carbonium ions, then induces dissociation among ortho protons; eventually generating new ectopic CCDB mixed olefin with certain cis/trans (Z/E) ratio in terms of thermodynamically stable.

Since the 1930s, Ipatieff et al. [2] studied isomerization of butene using various catalysts such as phosphoric acid, perchloric acid, toluene-p-sulfonic acid and zinc chloride solutions, shown in **Figure 2**. In the 1960s, F. Asinger and his co-workers [3] catalyzed isomerization of α -undecene to form internal undecene with homogeneous catalyst like sulfuric acid, perchloric acid and other moderately strong acid, respectively, shown in **Figure 3**.

**Figure 2.**

C=C isomerization in butene.

**Figure 3.**

C=C isomerization in α -undecene.

α -alkenes can be isomerized into mixed internal olefins isomers under appropriate solvents systems, acidity, temperature, and other reaction conditions that enhance catalysis. As a catalytic system, perchloric acid/anhydride can promote isomerization of α -undecene under 100°C in a high conversion rate with few side reactions (mainly oligomerization) [3]. Other Lewis acids such as boron (tri)fluoride (BF₃), aluminum chloride (AlCl₃), and borofluoric acid (HBF₄) were used to catalyze α -undecene to lead to more α -undecene oligomerization in even less time. However, acidic catalysts used inhomogeneous reactions like those mentioned above are hard to recycle and high in attrition rate. Therefore, recent research mainly focuses on using solid acids Al₂O₃, SiO₂, WO₃, Al₂O₃-SiO₂, mesoporous Ti, Nb and Ta oxides, etc., on performing the acidic olefin isomerizations, which are heterogeneous catalysts [4–8]. Their catalysis efficiencies depend on their acidity in general. To increase the surface acidity and catalytic activities of these heterogeneous catalysts, researchers covered them, aluminum oxides/salts or silicon/silica, by a various set of materials as follows: (1) proton acids (sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid, boric acid, hydrofluoric acid); (2) Lewis type acids (AlCl₃, SbF₅, BF₃, and P₂O₅); (3) ammonium salts (NH₄F). (4) Strong chlorinating agents (PCl₃ and PCl₅); (5) a strong Lewis acid like CH₃AlCl₂; (6) molecular halogens (Cl₂ and I₂) [4].

AlCl₃, as a Lewis acid, is a problematic catalyst for CCDB isomerization of alkenes which forms more by-product, requires large dosage of catalysts and hard to recycle. Acid sites in γ -Al₂O₃ as an amphoteric oxide can be used as catalytic center to catalyze isomerization of α -molecule to promote CCDB's migration and cis-trans isomerism, while non-acidic sites in catalysts can promote other side reactions such as alcohol dehydration; As a heterogeneous catalyst, SiO₂-Al₂O₃-MgO promoted 1-butene isomerized to both cis- and trans-2-butene with the isomerization taking place via π -complexes on the acidic sites of the catalysts, which are easy to be separated from reaction system, thus gradually replacing the homogeneous catalysts to be applied in olefin isomerization (**Table 1**).

Among metals oxide listed in **Table 2**, either sulfated mesoporous Nb oxides (C₁₂H₂SO₄ Meso Nb) or Ta oxides (C₁₂H₂SO₄ Meso Ta) showed higher activities and selectivity than sulfated mesoporous Ti oxides (C₁₂H₂SO₄ Meso Ti), Amberlyst 15, HY zeolite and H-ZSM5 in CCDB isomerization of 1-hexene. The conversion rate of 1-hexene to trans/cis 2-isomers reaches 95.89% when using C₁₂H₂SO₄ meso Ta as catalysts in 4 hrs was reported. And the ratio of trans/cis isomers reaches up to 3.7 after 6 hrs, shown in **Figure 4**. C₁₂H₂SO₄ meso Ta showed both high activity and selectivity, which can be attributed to its high BET surface area (292.19 m²·g⁻¹),

Sample	pH	Acid amount (mmol·g ⁻¹)
C ₁₂ Meso Ti	+3.3	2.0
C ₁₂ H ₂ SO ₄ Meso Ti	+0.8	4.7
C ₁₂ Meso Nb	-6.6	2.4
C ₁₂ H ₂ SO ₄ Meso Nb	-8.2	31.7
C ₁₂ Meso Ta	-6.6	0.4
C ₁₂ H ₂ SO ₄ Meso Ta	-8.2	19.8
HY Zeolite	-6.6	1.5
H-ZSM5	-4.4	16.1
Amberlyst 15	N/A	N/A

Table 1. Acid strength and acid amount of solid acid catalysts (measured by Hammett indicators and *n*-butylamine titration) [9].

Material	Xi (%)	Si (%)	TOF × 10 ³ (s ⁻¹)
SAC-13	82	65	36
XZO 1251	51	55	27
XZO 1251 ^a	98	-30	120
SAPO-11	74	83	2.3
ZSM-35	74	66	4.1
K2620	79	70	0.81
AM-15 ^b	23	78	0.41
AM-35	74	76	0.75
AM-70	7.1	24	0.062
AM-XN1010	74	43	1.3
BCPR4	4.2	31	1.3
BCPR5	15	74	4.2
BCNA2	0	N/A	0

^a185°C^b110°C

Xi: Conversion to internal alkene;

Si: Selectivity to internal alkene;

TOF: Turnover frequency based on the measured acid site densities are defined by Eqs. (1)–(3).

$$Xi = \left(1 - \text{mol} \left(\frac{\text{Terminal, Product}}{\text{mol(Terminal, Feed)}} \right) \right) \times 100\% \quad (1)$$

$$Si = \frac{\text{moles(Target, Product)} - \text{moles(Target, Feed)}}{\text{moles(Target + Branched + 2 \times Dimer, Product)} - \text{moles(Target + Branched + 2 \times Dimer, Feed)}} \times 100\% \quad (2)$$

$$\text{TOF} = \frac{Xi(\%)}{100\%} \times \left(\frac{\text{mLC}_{16}}{\text{min}} \right) \times \left(\frac{0.783\text{gC}_{16}}{\text{mLC}_{16}} \right) \times \left(\frac{\text{molC}_{16}}{224\text{gC}_{16}} \right) \times \left(\frac{\text{g catalyst}}{\text{meq}} \right) \times \left(\frac{1}{\text{g catalyst}} \right) \times \left(\frac{1000 \text{ meq}}{\text{mol}} \right) \times \left(\frac{1 \text{ min}}{60\text{s}} \right) \quad (3)$$

The TOFs in **Table 2** were determined from the calculated first-order rate constants, although in practice these numbers are very similar to what is found using Eq. (3).

Table 2. Isomerization of α -hexadecenes catalyzed by solid acid catalysts listed [10].

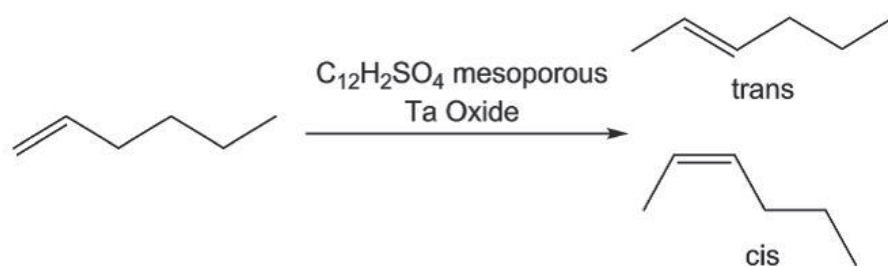


Figure 4. C=C isomerization in α -hexene catalyzed by $\text{C}_{12}\text{H}_{20}\text{SO}_4$ mesoporous Ta oxide.

optimal pore size (18.2 Å), and increased concentration of active Brønsted acid sites on the surface of the mesoporous channels [8].

Heteropoly acids (HPAs) are a unique type of materials that are active both in oxidation–reduction and acid catalysis [9, 11, 12]. The polyoxometalates form heteropoly anions with metal-oxygen octahedra and work as the basic structural unit. The Keggin-type HPAs are the most important in catalysis: the Keggin heteropoly anion has the empirical formula, $\text{XM}_{12}\text{O}_{40}\text{n}^-$, wherein X is a non-metal heteroatom (e.g. P^{5+} , Si^{4+} or B^{3+}) and M is a metal addenda atom (e.g. MO, W, V, Ce, Zr, Nb, Sb and Ti). Exemplary Keggin heteropoly acids in which X is phosphorus. 12-tungstophosphoric ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, TPA) is the most usual catalyst of choice because of its high acidic strength and relatively high thermal stability. They are strong Brønsted acid catalysts, and are stronger than conventional solid acids like zeolites and mixed oxides.

HPAs can be used either directly as a bulk material or with the supports. The supported form is preferable because of relatively higher surface area compared with the bulk material ($5\text{--}8\text{ m}^2\cdot\text{g}^{-1}$) and better accessibility of reactants to the active sites, on the premise that carriers have little interaction with HPAs. Solid carriers, including acidic (silica, acidic ion-exchange resin) and neutral solids carriers (active carbon), have been reported that are suitable as HPA supports. The molecular structure is shown in **Figure 5**.

Zhiping Du et al. [12] used HPAs supported by Al_2O_3 to catalysis on isomerization of 1-hexene to 2-hexene, 3-hexene, and 1-octene to 2-octene, 3-octene, 4-octene, etc. They investigated the influence of catalyst dosage, time, temperature, reactant purity, activation conditions of the HPAs, and supporting materials on the isomerization efficiency of 1-hexene and 1-octene. Their study showed that HPAs could promote olefin isomerization under a low temperature that CCDB migration and cis-trans isomerization take the main place with little skeleton isomerization.

However, HPAs catalysts for CCDB isomerization of alkenes are not perfect and do have it own problems. A typical issue is the thermal stability of HPAs wasn't high enough for conventional regeneration by the burning of coke at $500\text{--}550^\circ\text{C}$ as routinely used in the case of zeolites and aluminosilicates because susceptibility of these types of catalysts to deactivation during organic isomerization reactions due to the formation of carbonaceous deposits (coke) on the catalyst surface.

Cation exchange resin (CER) [13–20] is a type of solid catalysts in which its catalytic mechanism is the same as homogeneous catalysts, while it does have active sites like silica gel, Al_2O_3 , and zeolite as carriers, brings to CER become a pseudo homogeneous system. CER is used to catalyze gaseous short-chain alkene isomerization ($\text{C}_4\sim\text{C}_7$). For example, α -butene could be isomerized to form certain cis/trans ratio 2-butene with yields up to 90% [10, 21–29]. In general, advantages of

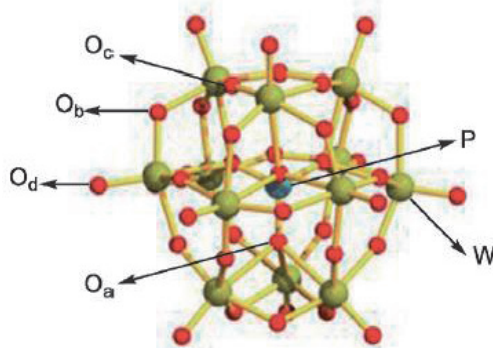


Figure 5.
The structure of 12-tungstophosphoric acid.

CER are: (1) it can be made in different shapes, structures and load capacities for different application purposes; (2) active groups are usually located on the surface of internal holes of CER, which is easy to contact with olefin molecular with faster reaction rate and higher yields; (3) catalysts are pseudo homogeneous, which means separation between catalysts, reactants and products are easier than homogeneous catalysts, for instant, homogenous acid catalysts have to deacidify after the reaction; so that bring to (4) catalyst may be reused for several times to avoid waste liquid's pollution to environment.

3. Basic catalysis

In base catalysis of olefin isomerization, α -alkenes or their derivatives (1) form secondary (or tertiary) carbanions with the base anions (B^-), then (2) rearrange into more stable primary carbanions, which (3) react with base (BH) to form new internal alkenes or their derivatives.

Forming cis-isomers is preferred in base-catalytic isomerization because the allyl intermediate is generated by losing protons from the olefin, and cis-isomer is more stable than trans-isomer.

The Shell Higher Olefin Process (SHOP) is a well-known and important base catalytic method that the Royal Dutch Shell commercialized in 1977 to produce α -olefins with controllable length from ethylene and subsequently to manufacture the corresponding aldehydes and fatty alcohols for producing detergents and surfactants [30]. The SHOP process incorporates the following reactions: oligomerization (Figure 6) [30], double bond isomerization (Figure 7a), and metathesis (Figure 7b) [30–32].

Some long chain alkenes isomerization, like isomerizing α - $C_{34}H_{68}$ to 11- $C_{34}H_{68}$, is industrially accomplished by Na/K loaded Al_2O_3 catalyst, or MgO, under reaction temperature at 80–140°C and pressure at 0.34–1.72 MPa [30–32]. The conversion rate of α - $C_{34}H_{68}$ into 11- $C_{34}H_{68}$ is more than 90%. Then subjected to the metathesis reaction, and in which catalysts comprising an alkali metal such as sodium, potassium dispersed on a high surface area, mainly inert, solid supporter, such as Al_2O_3 were prepared at the temperature between 5 and 50°C and in the molecular-oxygen-containing activating gas of oxygen-to-alkali ratio of 0.01–2 [31]. In the other case, catalyst on CCDB isomerization were those that have little

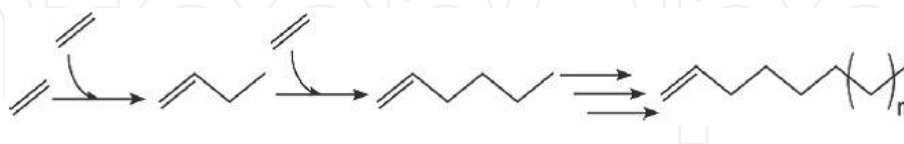


Figure 6. Oligomerization of ethylene by Ni catalysts under 80–120°C, and 1000–2000psig.

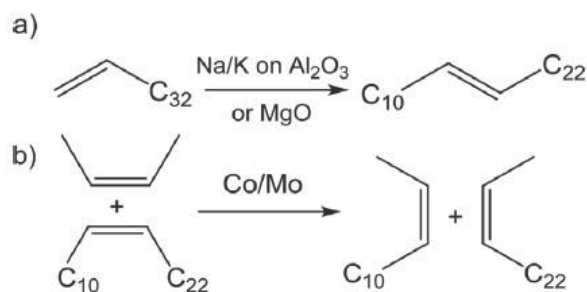


Figure 7. SHOP process steps: a) alkene isomerization and b) metathesis.

polymerization and cracking, and include supported bauxite, alumina supported cobalt oxide or iron oxide or manganese oxide, and so on [32].

Under the conditions like that of isomerization, higher molecular like 11-C₃₄H₆₈ reacted with lower molecular like butadiene in metathesis reaction to produce a mixture of olefins such as internal C₁₃H₂₆, and C₂₅H₅₀, which are for chemical intermediates required by surfactants and detergents. The oligomerization of ethylene by Ni catalysts in the SHOP process was showed in the follows as **Figure 8** [18].

The industrial manufacturing of co-monomer ethylidene norbornene (ENB) also utilizes the alkene isomerization [33]. The reaction pathway is using Na-loaded-Al₂O₃ catalyst to the vinyl norbornene, produced from a Diels-Alder reaction, which deprotonated, rearranged, and reprotonated into the ENB (**Figure 9**).

Sumeet K. Sharma et al. [34] studied the selective double bond isomerization of allyl phenyl ethers catalyzed by ruthenium metal complexes, achieve a conversion rates of methyl chavicol (99.7%) with 95.4% selectivity of trans-anethole and eugenol (99.8%) with 95.6% selectivity of trans-isoeugenol in ethanol using RuCl₂(PPh₃)₃ catalyst. Ruthenium catalysts [35, 36] are relatively expensive, although they present an extraordinary performance on catalysis efficiency, the potential of massive production are very gloomy. On the other hand, inexpensive

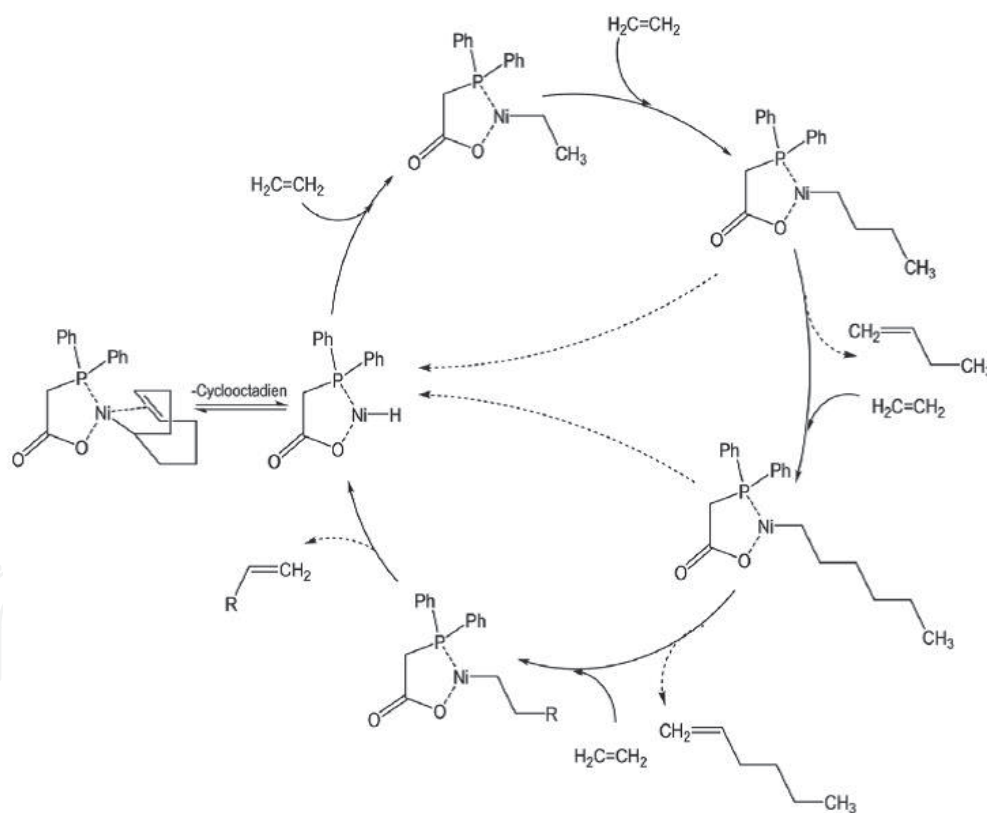


Figure 8.
The oligomerization of ethylene by Ni catalysts of the SHOP process.

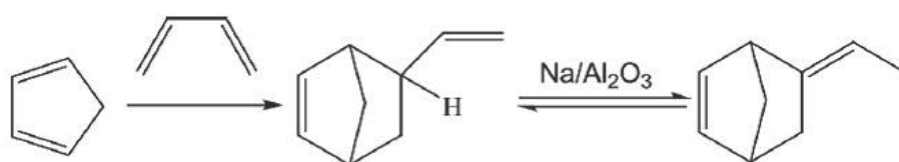


Figure 9.
Ethylidene norbornene formation by catalyzed isomerization of vinyl norbornene.

transition metals catalysts usually have a poorer performance, but it is more likely for industrial scale production after enhancing their efficiency.

Jiraporn Puriwat et al. [37] studied the gas-phase isomerization of 1-butene to 2-butene on the MgO/Mg(OH)₂ catalysts containing different basicity sites (i.e. weak, medium, and strong basic sites). The isomerization reactions mainly occur on either the strong or the medium-strength basic sites. In fact, the weak basic sites had little impact on the isomerization activity. The crystalline MgO contained both weak and strong basic sites, while the Mg(OH)₂ phase exhibited only the medium strength sites. In the lattice of crystalline MgO, strong basic sites are coming from the presence of oxygen atoms. The medium strength basic sites in Mg(OH)₂ risen from the hydroxyl groups in the Mg(OH)₂ structure.

Some strong base, like KOH [38], can be used independently in DMSO or alkoxide system, to catalyze position isomerism of propenyl C=C, to produce the intermediate could be applied in the perfume, cosmetic, pharmaceutical, and materials chemistry, and also as intermediates in synthetic sequences for the construction of more complex products. KOH, or NaOH was also a catalyst on C=C isomerization of allyl aromatics estragole and eugenol. Allyl aromatics estragole and eugenol could further turn into the corresponding alkenyl aromatics trans-anethole and trans-isoeugenol, respectively. Under certain conditions, 56% conversion was achieved with modest E:Z in 12 hours. This methodology does have drawbacks including the following as: the use of strong base in stoichiometric amounts, longer reaction times, incomplete conversion of reactant, low selectivity for the trans-isomer, high temperatures, caustic waste, and the likely need to separate the cis-isomer [39, 40].

4. Molecular sieves

According to the carrying amount of acid sites or alkaline sites, the molecular sieve can be divided into acid catalyst and base catalyst. Due to their unique structures and a broad prospect in industrial application, taking molecular sieves as an option is unavoidable for studies on catalysis that would like to apply their finds on an industrial scale. For the CCDB isomerization of alkenes, molecular sieves can be further subdivided into zeolite and non-zeolite catalysts. Non-zeolite molecular sieve are those formed by metal skeleton compound MOF, SAPO, etc. [41, 42].

Hu et al. [40] reported that mesoporous molecular sieve supported vanadium catalysts such as V-MCM-41, V-SBA-15 and V-TUD-1 with different pore structures and pore sizes were prepared via a post-synthesis grafting method using atomic layer deposition, by means of which the isomerization of 1-heptene was employed as a reaction probe to characterize the acid properties of these catalysts with moderate acid strengths. The results were that conversion yield as high as 92% at 600 K and isomer selectivity over 90% (mainly double bond shift products) over the V-SBA-15 catalyst were achieved.

Gajda et al. [41–45] developed a series of non-zeolite molecular sieve (NZMS) in succession in 1990s. The composition of synthetic molecular sieves, pore structure, and active component distribution at molecular level is controllable. It successfully catalysis CCDB isomerism of α -butene, α -pentene and other short-chain olefin, to produce tertiary olefins, which can be used to make high octane ether compounds required by reformed gasoline. The preferred NZMS were the silicoaluminophosphate molecular sieves described in the patent [42], which are disclosed as microporous crystalline silicoaluminophosphates. They have a three-dimensional microporous framework structure of PO_2^+ , AlO_2^- and SiO_2 tetrahedral units, and whose empirical chemical composition on an anhydrous basis is:



wherein “R” represents at least one organic templating agent presented in the intracrystalline pore system; “m” represents the moles of “R” present per mole of $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$ and has a value of from 0.02 to 0.3; “x”, “y” and “z” represent the mole fractions of silicon, aluminum, and phosphorus present in the oxide moiety. Gajda et al. [46, 47] further developed a method to increase the proportion of isobutene with less by-products, by using a catalyst comprising at least one NZMS, which contains framework tetrahedral units (TO_2) of aluminum (AlO_2), phosphorus (PO_2), and at least one additional element (EL) as a framework tetrahedral unit (ELO_2).

A NZMS made up by Ferroaluminophosphates are also presented in patent [48], which has a three-dimensional microporous crystal framework structure of AlO_2 , FeO_2 and PO_2 tetrahedral units, and whose empirical chemical composition on an anhydrous basis is:



Or the NZMS were crystalline microporous aluminophosphates in which the substituent metal is one of a mixture of two or more divalent metals of the group magnesium (Mg), manganese (Mn), zinc (Zn) and cobalt (Co), presented in patent [49], whose empirical chemical composition on an anhydrous basis is:



Or the NZMS were the MnAPSO molecular sieves [50] which have a framework structure of MnO_2 , AlO_2^- , PO_2^+ and SiO_2 tetrahedral units whose empirical chemical composition on an anhydrous basis is:



Zeolite catalysts are aluminosilicate salts, depending on their pore structures and adjustable acidities, they could be divided into X-, Y-, ZSM-5, β -type, etc. [51, 52].

5. Organometallic “chain-walking” catalysts of transition metal

Depending on the element they used, transition metal catalysts can be classified as noble metal catalysts or non-noble metal catalysts. Noble metals, by definition, are metallic elements distributed in group VB, VIB, VIIB, and VIII. Typical examples are Pd, Ru, Rh, Ir, Os, etc. [38, 53–60]. Their complex compounds catalyze the isomerization by converting the double bonds of the α -alkenes to the β and γ positions, which is different from the acidic catalyst that catalyzes the isomerization reaction by converting the double bonds of both α - and β -alkenes to internal positions further. It also promotes side reactions that include cracking, oligomerization, skeletal isomerization, and alkylation.

Noble metal catalysts, however, are expensive and unrecyclable, which limited their application in the industry. While some common metals like Fe, Cu, Zn, Co, etc. [38, 61–64] are much cheaper and can promote C=C migration of α -linear olefins to generate internal olefins in high efficiency, too, providing another option. For example, CoCl_2 and Grignard reagent can isomerize α -tetradecene to generate (E)-2-, (Z)-2-, 3-tetradecene, and other isomers under 50 Celcius degree [38]. Also, Fe and Co complex compounds can shift the position of the C=C on the allyl benzene side chain, isomerized, and generated into various allyl benzene

intermediate. These can be used as intermediate of perfume, antibiotics, insecticides, anti-Leishmania drugs, antifungal, algae inhibitors, anti-inflammatory drugs, antioxidants etc., which leads to a strong industrialized potential.

6. Photocatalysis

In 1983, the photocatalytic carbonylation synthesis reaction of aromatic halogenated hydrocarbons was realized, leads the dawn of the application of photocatalysis in organic synthesis. In the few decades, photocatalytic ring-opening polymerization and photocatalytic epoxidation of olefins have been reported, which makes photocatalytic organic synthesis has become an important branch in the field of photocatalysis. Comparing to the thermal catalysis, photocatalysis reactions are relatively environmental friendly, requiring more mild reaction conditions, different selectivity of isomers' structures. These advantages provide some special merits that brings more options when chooses the reaction routes for both academic studies and industrial manufacturings.

Cirjak and his co-workers [65] used metal clusters $(C_5R_5)_aFe_bM_c(CO)_dL_e$ as the photocatalyst to catalysis isomerism of olefin, in which the catalyst's absorption wavelength covers up to 220 nm with a low yield. Except for catalysis on CCDB position migration isomerism of alkenes, some photocatalysts such as Pd@TiO₂, could shift the allylic C=C position of the allyl aromatics along allyl chain to form isomers [66]. $[HFeM(CO)_8L^-]$ or $Fe(CO)_5$ can be used as photocatalyst in THF to catalyze 1-allylbenzene at room temperature under illumination conditions, isomerized into 2-allylbenzene [67]. Under mild conditions, the reaction productivity is over 98%, and the E/Z ratio in product is 10:1 which is a decent selectivity.

Recent years, Ma et al. [68] discovered a series of solid heteropoly acids and their supported zeolite sieves as photocatalyst to catalysis on CCDB isomerization of alkenes. A small amount of catalysts shows a strong catalytic activity on C=C isomerization of linear chain α -olefin (C₅-C₂₀) into internal olefins under visible light, in which the conversion rate can be up to 80% in 1 hour, and presents a high isomer selectivity (either E or Z). It was perfectly avoiding the complicated separation of E&Z isomers which is important for some purposes, like pharmaceutically, which do require isomer selectivity. Under ultraviolet irradiation, the catalysts to oleic acid (CH₃(CH₂)₇CHCH(CH₂)₇COOH, cis), priority to generate 3-trans-, 6-trans-, 11-trans-octadecenic acid and so on, with the conversion rate being up to 80% in 1 hour. The catalytic system also can catalyze a series of phenylpropyl compounds to make CCDB isomerization under ultraviolet irradiation, mild temperature and ordinary pressure to produce certain location isomer, which were widely used in production of high value chemical products applied in the field of medicine, biology and materials science, as shown in **Figure 10**.

This type of multifunctional catalyst combined four catalysis: photocatalysis, acid catalysis, molecular sieve catalysis and transition metal catalyzers which synergistically worked to promote C=C double bond migration of olefins and its derivatives. The main problems are as following: narrow catalysis absorption wavelength range, which was mainly in ultraviolet and near ultraviolet regions, low utilization of solar energy; the recombination rate of photo-generated carriers and hole is high, which results in lower quantum efficiency. Thus, we need to modify the structure and component of catalysts at present, such as the control of catalyst's crystal structure and defects, adjusting the energy band location and surface photosensitization etc.

However, photocatalysis on olefin's isomerization is not well-known enough which has to clarify the photocatalytic reaction mechanism, especially photo

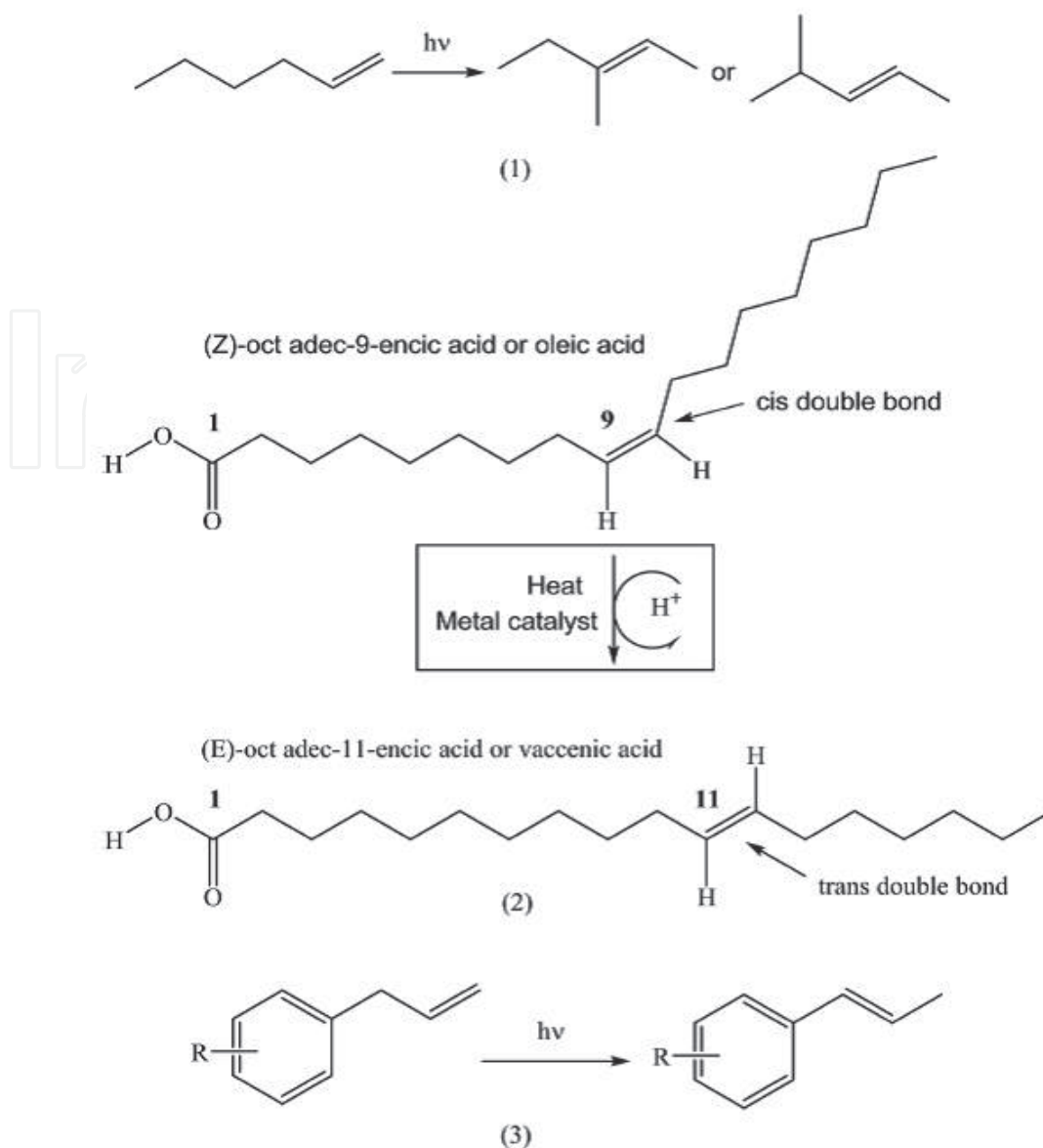


Figure 10.
CCDB isomerization of straight chain alkenes (1), oleic acid (2) and Allyl benzene (3).

generated carrier separation, transfer and interface shift process, that are essential to further improve the catalytic efficiencies. On another hand, future works may take advantages from some well-studied photocatalysis fields like nanomaterials, semiconductor physics, and photocatalysis organic reaction, to produce novel photocatalytic materials with high efficiency and high catalytic activity.

7. Conclusions

In this paper we summarized olefin isomerization catalysis in five categories, acidic, basic, molecular sieve, transitionmetal catalysis, and photocatalysis, and under each category, we present some typical catalysts that have been studied. The five categories differentiates most available catalysis systems by their reaction mechanisms, and they also reflect somehow their properties, like acidic catalysis usually have issues on products selectivity and catalysts recycling. The **Table 3** followed presents all catalysis systems mentioned before, what they are, which category they belong to, applicable reactants and desire products, with their purposes and features, pro and cons, and references of the works.

Method	Catalysis System	Olefin and Derivatives	System Features	References
Acidic Catalysis	H ₂ SO ₄ , HNO ₃ , HCl, H ₃ PO ₄ , p-H ₃ C-C ₆ H ₄ -SO ₃ H, C ₆ H ₅ -SO ₃ H	Linear α -olefins (C ₄ -C ₂₀)	Brønsted Acid, homogeneous catalysis, high reaction rate, conversion rate, selectivity; Poor to recycle, corrosive	[3]
	BF ₃ , HBF ₄ , Tetramethylene sulfone		Lewis Acid, high reaction rate and conversion rate; may causes polymerization of olefins; highly toxic, inflammable, poor to recycle, corrosive	[3]
	AlCl ₃		Mild reaction rate, conversion rate, and selectivity, inexpensive; may causes polymerization of olefins; heavy dosage, poor to recycle	[3]
	Sulfided ion exchange resin		Gas-phase reaction, isomerizing both cis- and trans- β olefins; incapable of long liner olefin isomerization	[5-8, 11, 25-29]
	Cation exchange resin, perfluorinated ion exchange resin		Robustness to deactivate, longevity; slow reaction rate, side reactions	[10, 13-18]
Basic Catalyst	Al ₂ O ₃ , SiO ₂ , WO ₃ , ZrO ₂ , TiO ₂ , Nb ₂ O ₅ , Ta ₂ O ₅ , and heteropoly acids	Linear α -olefins (C ₄ -C ₇)	Lewis Acid, slow reaction rate, conversion rate, poor selectivity, heterogeneous catalysis. Heteropoly acids	[21-24]
	Na/K-Al ₂ O ₃ , MgO	α -C ₃₃ H ₆₆	The Shell Higher Olefin Process (SHOP) industrial catalyst, reaction isomerized 11-C ₃₃ H ₆₆ , conversion rate >90%	[30]
	γ -Al ₂ O ₃ -NaOH-Na, γ -Al ₂ O ₃ -Na ₂ CO ₃ -Na	Linear α -olefins	Good reaction rate, conversion rate, and selectivity; high temperature required	[30]
	Na-Al ₂ O ₃ , Potassium tert-butoxide, Ti-Ziegler (X ₃ TiH)	Vinyl Norbornene	Ethylene C=C positional transfer, industrial catalyst in use	[35]
	Strong base like KOH; KOH/DMSO; other hydroxides/alcohol-salt system	Propenyl aromatic compounds	Promote internal movement of C=C on propylene to form allyl compound; wild applied in perfume and food industry; long reaction time, low conversion rate, hard to purify	[38]
Molecular Sieve Catalysis	0.83Na ₂ O-1.00Al ₂ O ₃ -2.48SiO ₂	α -olefins (C ₆ ~C ₂₅)	>70% conversion rate in short time under room temperature; low side reaction; longevity catalyst lifetime	[39]
	Mesoporous molecular sieve like MCM-41, SBA-15, and TUD-1		92% conversion rate and 90% selectivity using V-SBA-15 to catalysis α -octene isomerization under 600 K	[40]
	Non-zeolite molecular sieve (MZMS); MOF-mR: (Si _x Al _y P _z)O ₂	1-butene	Synthesis isobutene and 2-butene under 200~600°C	[41]

Method	Catalysis System	Olefin and Derivatives	System Features	References
	Non-zeolite molecular sieve(MZMS); MOF-mR: (Si _x Al _y P _z)O ₂ MZMS mR: (M _x Al _y P _z)O ₂ , M=Co, Fe, Zn, Ca, Mn, etc.	1-butene 2-butene	Synthesis isobutene and 2-butene under 200~600°C Synthesis 1-butene and isobutene, could be further used to obtain ether for reformulated gasoline	[43]
	NZMS	1-butene 1-pentene	Isomerizing into isobutene, few side products.	[44–49]
	NZMS SAPO-11	1-hexene	Reinforce positional isomerism instead of cis-trans isomerism	[50]
	Zeolite molecular sieve: X, Y, ZSM-5, etc.		Isomerizing 1-hexene into 2- and 3-hexene	[51, 52]
Transition Metal Catalysis	Pd black/PdCl ₂	Linear α-olefins, ketenes	A industrialized catalyst to isomerizing α-olefin into stable, internal form. Expensive, toxic, complicate for further processing	[53]
	Ru ₃ (CO) ₁₂ , Ru ₃ (CO) ₁₁ ((2-pentenyl)PPh ₂), [Ru(CO) ₂ (MeCO ₂) ₂] _n , [Ru(CO) ₄ (μ-MeCO ₂)(CH ₃ CN) ₂], [Ru ₂ (CO) ₄ (μ-MeCO ₂) ₂ (μ-dppm) ₂ PF ₆]	Linear α-olefins	Could isomerize 1-pentene into 2-petene in benzene solution at 80°C	[34–38]
	Os ₃ (CO) ₁₂ , Co ₂ (CO) ₈ , Mo(CO) ₆		Could isomerize 1-pentene into 2-petene in benzene solution at 80°C	
	CoCl ₂ , Grignard reagents with ligands			
	Fe(CO) _n (n=5,9,12...)	Vinylene olefin	Forms di-substituted internal olefin under 150~350°C with a minor amount of tri-substituted internal olefin	[61]
	Fe ₃ (CO) ₁₂	3-ethyl-1-pentene	Forms 3-ethyl-2-pentene at 25°C, 12 hrs	[62]
	RhCl ₃ H ₂ O/Methanol/Ethanol; RhCl ₃ /OH ⁻ ; [Rh(OH)-(COD)] ₂	Propenyl aromatic compounds	A very original application study of using Rhodium in C=C migration	[34, 61, 62]
	Ir(H) ₂ X-(PtBu ₂ Ph) ₂ , X=F, Cl, Br, I, OH or OCH ₂ CF ₃ , polymer carried irdium catalysis system; R-[(PPh ₂) ₂ Ir(H) ₂ THF ₂] ⁺ PF ₆ ⁻		Propenyl C=C migration, intermediates of propenylbenzene with different subsituted functional group are essential materials for perfume, antibiotics, pesticides, etc.	[54, 55]
	RhCl ₃ 3H ₂ O/Ethanol, RhCl ₃ 3H ₂ O/PF ₆ -Methanol; RuCl ₂ (PPh ₃) ₂ , carried by sol-gel method			[56–58]
	Na ₂ Fe(CO) ₄ /CuCl or BrCH ₂ CH ₂ Br			[63]
	HCo(CO) ₄			[64]

Method	Catalysis System	Olefin and Derivatives	System Features	References
Photo Catalysis	Metal Cluster Compound	Internal Olefin (C ₄ ~C ₂₀)	(CnRn)aFebMc(CO)dLe, M=Mo, Ru, Rh, Sc, Ti, Cr, Mn, Co, Ni, Cu, Zn. L=V group ligands. Higher	[65]
	Pd@TiO ₂	Linear α -olefins	Day light, selective isomerism into E isomer.	[66]
	Fe(CO) ₅		Room temperature, day light, isomerizing 1-propenylbenzene into 2-propenylbenzene, good selectivity	[67]
	[HFeM(CO) ₈ L ⁻](M=Cr, Mo; L = CO)		Room temperature, day light, THF solution system, isomerizing 1-propenylbenzene into 2-propenylbenzene, conversion rate >98%, E/Z ratio = 10:1	
	Supported heteropolyacid catalyst	Linear α -olefins	Room temperature and pressure, visible light, fully conversion into internal olefin	[68]
Supported heteropolyacid catalyst	Oleic acid	Room temperature and pressure, visible light, fully conversion into Ω -3, Ω -6		

Table 3.
Catalytic system for olefin isomerization.

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Conflict of interest

The authors declare no conflict of interest.

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Author details

Wangjing Ma^{1*}, Bonan Liu², Duanda Wang¹, Jun Zhao¹, Lu Zhang¹ and Lei Zhang¹

1 Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China

2 State Key Laboratory of Heavy Oil Processing, China University of Petroleum (Beijing), Beijing, China

*Address all correspondence to: wjma@mail.ipc.ac.cn

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