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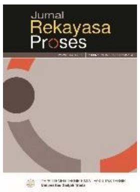

A Review on the Hydroisomerisasion of n-Parafins over Supported Metal Catalysts

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ABSTRACT

Catalytic hydroisomerization of n-paraffin aims to produce branched paraffin isomers and suppress cracking reactions in the production of the low cloud point of biodiesel. The development of the type of metal and catalyst support, amount of metal loading, and reaction conditions are important to increase the catalyst activity. A high performace catalyst for hydroisomerization bears bifunctional characteristics with a high level of hydrogenation active sites and low acidity, maximizing the progress of hydroisomerization compared to the competitive cracking reaction. In addition, a catalyst support with smaller pore size can hinder large molecular structure isoparaffins to react on the acid site in the pore thus providing good selectivity for converting n-paraffin. Catalysts loaded with noble metals (Pt or Pd) showed significantly higher selectivity for hydroisomerization than non-noble transition metals such as Ni, Co, Mo and W. The reaction temperature and contact time are also important parameters in hydroisomerization of long chain paraffin, because long contact times and high temperatures tend to produce undesired byproducts of cracking. This review reports several examples of supported metal catalyst used in the hydroisomerization of long chain hydrocarbon n-paraffins under optimized reaction conditions, providing the best isomerization selectivity results with the lowest amount of byproducts. The role of various metals and their supports will be explained mainly for bifunctional catalysts.

Keywords: geothermal silica; hydroisomerization; n-paraffin, supported metal catalyst bifunctional catalyst

ABSTRAK

Hidroisomerisasi n-parafin secara katalitik bertujuan untuk menghasilkan isomer parafin bercabang dan menekan reaksi perengkahan dalam pembuatan biodiesel yang memiliki titik awan rendah. Pengembangan jenis logam dan penyangga, jumlah muatan logam, dan kondisi reaksi penting dilakukan untuk meningkatkan aktivitas katalis. Katalis yang baik untuk hidroisomerisasi mempunyai ciri sifat dwifungsi dengan sisi aktif hidrogenasi yang tinggi dan

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keasaman yang rendah, sehingga dapat memaksimalkan berjalannya reaksi hidroisomerisasi dibandingkan dengan reaksi perengkahan. Selain itu, ukuran lubang pori penyangga yang kecil dapat membatasi isoparafin dengan struktur molekul yang besar untuk bereaksi di situs asam di dalam pori sehingga memberikan selektivitas yang baik untuk mengonversi n-parafin. Katalis yang dimuat dengan logam mulia (Pt atau Pd) menunjukkan selektivitas yang jauh lebih tinggi untuk hidroisomerisasi dibandingkan logam transisi non-mulia seperti Ni, Co, Mo dan W. Suhu dan waktu kontak reaksi juga menjadi salah satu parameter yang penting dalam hidroisomerisasi parafin rantai panjang, karena waktu kontak yang lama dan suhu yang tinggi cenderung menghasilkan produk samping hasil perengkahan. Kajian ini melaporkan beberapa jenis katalis logam berpenyangga yang digunakan dalam hidroisomerisasi hidrokarbon rantai panjang di bawah kondisi reaksi yang dioptimalkan, memberikan selektivitas isomerisasi terbaik dengan jumlah produk samping terendah. Peran berbagai logam dan penyangga akan dijelaskan terutama untuk katalis bifungsional.

Kata kunci: *hidroisomerisasi; katalis dwifungsi; n-parafin; penyangga katalis*

1. Introduction

Hydroisomerization of n-paraffin plays an important role in the petroleum industry (Sullivan et al., 2014). The role of hydroisomerization in fuel (C4-C7) is intended to produce fuel products with high octane numbers (Zhao et al., 2017). In the case of biodiesel or biofuel, hydroisomerization functions to reduce the melting point of long-chain esters by adding methyl branches to the hydrocarbon molecule chains to become branched-chain fatty acids (BCFA), thereby reducing the cloud point of the mixture (Maghrebi et al., 2021) and producing methyl esters with superior fuel stability (Oxidative Stability Index/OSI > 40 hours) and low melting point (<20 oC) (Loh et al., 2021). One way to make the pour point of biodiesel less prone to freeze is to isomerize their straight-chained n-paraffins into branched ones (isoparaffin) (Monirul et al., 2015; Reaume and Ellis, 2013), as it is known that n-paraffin is the first group that undergoes isomerization and cracking. Isomerization reaction generally occurs in bifunctional catalysts containing metallic sites for hydrogenation / dehydrogenation and acid sites for skeletal isomerization via carbenium ion (Aboul-Gheit et al., 2014; Jenie et al., 2010). The extent to which isomerization occurs depends on many factors such as the strength and number of acid sites, catalyst hydrogenation / dehydrogenation activity, surface area and pore size distribution as well as many process variables such as temperature, pressure, H2/n-paraffin ratio, and reactor type.

The use of silica-alumina as a catalyst for paraffin hydroisomerization has been widely used. The hydroisomerization of hexadecane using a metal-silica-alumina catalyst has been carried out by Regali et al. (2014), and because of its highly acidic nature, the Pt-Al-Si produces a fair amount of cracking product even at low conversion of n-hexadecane. The acidic site of silica is still weak, which is indicated by T max at 231 °C (Cecilia et al., 2013; Wu et al., 2014; Xin et al., 2016) and gives a low isomerization conversion rate (Liu et al., 2015), however, it demonstrates a fairly good selectivity (Wu et al., 2018). There have been many types of modifications to achieve an acid catalyst site, one of which is the sulfation of the supported catalyst. Sulfated zirconia has been investigated for the isomerization of various long chains, such as butane (Yang et al., 2018), pentane (Aboul-Gheit et al., 2014; Ejtemaei et al., 2017), and hexane (Bikmetova et al., 2016). High selectivity of light paraffin isomerization was obtained at low temperatures (de Barros et al., 2016).

In this review, several types of metal supported catalysts used in the hydroisomerization of long-chain hydrocarbons under optimized reaction conditions are reported, providing the best isomerization selectivity results with the lowest number of by-products. The roles of various metals and their supports will be explained in particular for bifunctional catalysts.

2. Catalysts Structure and Properties

2.1 Type of Catalyst Support and Acidity

The study of modification of the catalyst support with the addition of acidic compounds to increase the acid value of the catalyst on the hydroisomerization catalytic activity has been widely evaluated. The reaction mechanism of long-chain paraffin hydroisomerization is determined by the acidity of the catalyst (Batalha et al., 2015; Lee and Ihm, 2013). More acidic catalysts tend to experience excessive cracking resulting in yield loss, whereas less acidic catalysts do not catalyze the desired reaction, or only allow weak isomerization, resulting in the formation of long branched products with low octane amounts and low volatility.

Batalha et al. (2015) reported that Pt in beta acid zeolites has reaction mechanism that is thought to consist of several steps, namely parallel, reversible, and irreversible. With a decrease in acidity, the single-branch and bifurcated products, those which are still being produced, further react in parallel with the cracking products, whereas a sequential mechanism only occurs in the slightly acidic Pt-Beta (see Figure 1). Karthikeyan et al. (2016) found a greater number of product cracks in a series of mordenite catalysts than zeolite-β at all temperature ranges studied. The increased cracking activity of mordenite was caused by higher acid strength (0.218 mmol/g), whereas zeolite-β catalyst had a relatively low strong acid value (0.068 mmol/g) and did not have sufficient cracking capacity, so the cracked product was relatively lacking. Likewise, the total acidity of the SiO_2 material has a low and varied value, namely 0.078-0.084 mmol/g. The SiO_2 support only shows one peak corresponding to a weak acid site (Cecilia et al., 2013; Wu et al., 2014; Xin et al., 2016). This shows that the silica-alumina material has a good enough potential to support the hydroisomerization catalyst by producing a relatively low crack product.

Wang et al. (2020) found that adding sulfate ions to zirconia increased acidity, catalyzing the isomerization of alkane. In addition, the surface stability of the sulfate played an important role in increasing the isomerization activity. Gnanamani et al. (2012) proved that converting hexane with Pt/HfO_2-SO_4 catalyst was almost 100% but had low selectivity. High conversion percentage with low percent selectivity indicates continuous cracking, where the primary product remains adsorbed to the acid site to undergo a secondary cracking reaction which results in more isomer products with shorter chains and more branched isomeric products.

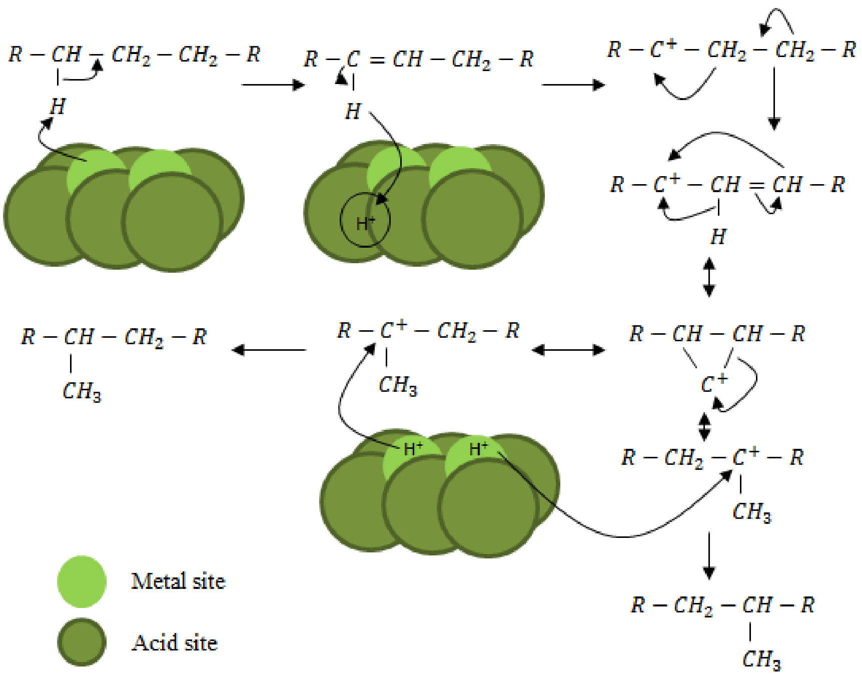

Figure 1. Plausible reaction mechanism of the hydroisomerization of long-chain n-paraffin over bifunctional catalysts (adapted from Bauer et al., 2014)

Bikmetova et al. (2016) conducted a study of n-hexane isomerization using Pt/SZ/SiO_2 catalyst by different amounts of impregnation. In the catalyst synthesized by single impregnation, the yield of i-hexane in the low temperature region was 10-20 wt%. This may be related to the low content of active components, especially sulfate ions in the catalyst. In the temperature range of 180-220 °C, the yield of i-hexane increased to 45-70 wt%. In the catalyst synthesized by double impregnations, the yield of isomers in the low temperature region increased to 45-55 wt%, and at 180-220 °C it became higher, namely 60-75 wt%.

The type of acid can also affect the catalytic activity of hydroisomerization. Gnanamani (2012) had conducted a study of the Lewis (L)/ Brønsted (B) acid ratio of the catalyst to the hydroisomerization activity. The results revealed that the catalyst with a higher L/B ratio had a higher activity for the n-hexadecane conversion. However, catalysts having more Lewis acid sites contribute more to cracking than the desired product isomer (Jaroszewska et al., 2021). Thus, a catalyst having a high hydrogenation activity and a low acidity is a good catalyst for maximizing hydroisomerization compared to cracking.

Yadav et al. (2009) observed catalysts supported by silica acid for esterification of aliphatic fatty acids. The support used was commercial silica, SiO_2-1, with a homogeneous spherical morphology and an average particle of 97 µm showing a high pore volume (3 cm^3/g) and diameter (24 nm) compared to SiO_2-2 support, with irregular morphology and a particle size of 141 µm (pore volume of 0.75 cm3/g, pore diameter of 6 nm). The study revealed that a homogeneous morphology, narrow particle size distribution, high surface area, and high pore volume resulted in a higher acidity. The decrease in the acidity of the calcined catalyst compared to the non-calcined catalyst can be ascribed to the breakdown of sulphuric acid to SO_3 and H_2O above 340 °C (Aboul-Gheit et al., 2012).

2.2 Type of Metal and Loading Amount

The role of the metal is to dehydrogenate the n-alkanes to form n-alkenes. The produced n-alkenes protonate on acid site to alkylcarbenium ions. These alkylcarbenium ions undergo skeletal rearrangement and β-scission follows by deprotonation and hydrogenation to alkanes form (paraffins). Heterogeneous catalysts has been investigated for catalytic hydrogenation by Kristiani et al. (2017). The result revealed that the use of catalyst supports plays an important role to increase the catalytic properties of heterogeneous metal catalyst in the hydrogenation, while the use of metal skeletal catalyst shows as a promising material for hydrogenation. Studies of bifunctional catalyst to isomerize n-paraffins by using precious metals and transition metals which are supported by various materials such as pore medium silicoaluminiphosphate/SAPO-11 (Tao et al., 2017), mesoporous silicoalumina (MSA) (Guanziroli et al., 2011), AlMCM-41 (Gao et al., 2019; Sobczak et al., 2012) have been widely done. However, there are still few publications applying metals other than Pt, such as Pd in SiO_2-Al_2O_3 support (Messou et al., 2016; Regali et al., 2014; Yu-Fen *et al.*, 2017). Catalysts loaded with precious metal (Pt or Pd) show much higher selectivity for hydroisomerization than those containing non-precious transition metals such as Ni, Co, Mo, and W (Pimerzin et al., 2019; Pimerzin et al., 2020). This may be because catalysts with transition metal charges form more coke than catalysts with precious metal charges (Tshabalala et al., 2021), in which the coke can be left in the acid site of the catalyst thereby disrupting the metal-acid site balance.

Comparison of the use of Pt/WO_3/ZrO_2 catalyst with various metal charges and operating conditions results in different hexadecane conversion and isomerization selectivity. The surface area of the catalyst appears to decrease with the increasing amount of WO_3. In addition, Gnanamani et al. (2012) reported that adding WO_3 to ZrO_2 (15% and 20%) decreases the total pore volume of the catalyst. The addition of more Pt and WO_3 metal loading to ZrO_2 was found to be reducing the percent conversion and selectivity of hexadecane hydroisomerization (Table 1). Aboul-Gheit et al. (2014) suggested that The Pt-Re/SZ catalyst has a different catalytic activity and selectivity hydro-isomerization compared to Pt/SZ and SZ catalysts, in which the conversion and the selectivity of pentane in the presence of Pt-Re/SZ catalyst are higher than that the presence of Pt/SZ or SZ catalysts. It might come due to a combination of metal loading. The main advantage of the bimetallic Pt/Re/SZ catalyst is its higher stability to catalyze the isomerization. However, the Ni metal loading shows a slightly different trend from the Pt metal. There is an increase in the conversion value and a decrease in the hydroisomerization selectivity of hexadecane as the amount of metal loading increase. The higher amount of Ni can increase the number of active site on the catalysts. The increasing hydroisomerization selectivity and cracking with the addition of more Ni is due to the presence of metal site on the acid site. Ion carbenium might be rapidly hydrogenated and transferred from the active site of alkanes

Table 1. Effect of surface area and metal loading on C16 conversion and selectivity

Catalysts	Metal loading	WO_3/ZrO_2 (%W)	Surface area ($m^2.g^{-1}$)	Conversion *n*-C_{16} (%wt)	Selectivity *i*-C_{16} (%wt)	References
1	0.5%wt Pt^{a}	11.83	74	97.3	4.1	Busto et al., 2012
2	0.5%wt Pt^{b}	8	74.9	94	51.4	Zhang et al., 2001
3	0.5%wt Pt^{b}	6.5	67.5	85.9	83.1	Zhang et al., 2001
4	1%wt Pt^{c}	14.85	47.2	84	45.6	Gnanamani et al., 2012
5	2%wt Ni^{b}	8	75.2	76	41.7	Zhang et al., 2001
6	5%wt Ni^{b}	8	71.7	90.8	34.4	Zhang et al., 2001

^{a}T 498 K, P 20.3 bar, WHSV = 18.4 h^{-1}, H_2/n-hexadecane = 10.0

^{b}T 503 K, P 20.7 bar, WHSV = 1.0 h^{-1}, H_2/n-hexadecane = 2.0

^{c}T 503 K, P 21.5 bar, WHSV = 1.0 h^{-1}, H_2/n-hexadecane = 2.0

before cracking occurs. Thus, to maximize the yield of isomers and suppress the cracking reactions, the catalyst needs to exhibit equal amounts of metal and acid site. Basically, high metal dispersion facilitates selectivity for hydroisomerization (Parmar et al., 2015; Wang et al., 2015). Several factors determine metal dispersion, namely metal loading, the type of precursor, and the method of catalyst preparation (Lee et al., 2014; Wang et al., 2015).

2.3 Pore Size of Catalyst

The pore opening of porous catalyst can also have a large effect on the selectivity of the catalysts. If the pore holes are small enough to limit the isoparaffin, which is larger than reacting at the acid site inside the pore, then the catalyst will show good selectivity to convert n-paraffin (Merabti et al., 2010). Table 2 shows the zeolite pore size information. Medium-sized zeolite pores (5-7 Å) prefer the formation of methyl branches in straight chains of aliphatic hydrocarbons. In general, the methyl branch increased with decreasing pore width of the zeolite, whereas the ethyl and propyl branched isomers that are more susceptible to hydrocracking are obtained from wide pore openings and large cavities.

Table 2. Information on zeolite structure and yield of i-C10

Zeolite catalyst	Index type / Topology	Pore size (Å)	Yield i-C10 (%wt)^{c}	
			mono-branched	multi-branched
Beta	BEA	5.7×7.5; 5.6×6.5^{a}	65	35
Mordenit	MOR	6.5×7^{a}	73	27
Y	FAU	7.4^{a}	n.a.	n.a.
USY	FAU	7.4×7.4^{a}	65	35
SDUSY	FAU	7.4×7.4^{a}	n.a.	n.a.
ZSM-22	TON	4.5×5.5; $5.7 \times 4.6^{a,b}$	91	9
ZSM-23	MTT	5.2×4.5^{b}	n.a.	n.a.
ZSM-35	FER	3.5×4.8; 4.2×5.4^{b}	n.a.	n.a.
ZSM-48	MRE	5.6×5.3^{b}	80	20
SAPO-11		3.9×6.3^{b}	81	19

^{a} Meir et al., 1987

^{b} Zhang et al., 2016

^{c} Yield i-C10 5% at 4.5 bar, 300 °C, H_2/n-C10 ratio: 214, WHSV 0,37 h^{-1} (Mota et al., 2013)

The high isomerization selectivity and low cracking of ZSM-22 have been reported due to the limitation of carbenium, which can enter the micropore opening of the zeolite, thus preventing the cracking reaction of the β-scission mechanism (Merabti et al., 2010). The pore medium size (ZSM-5 and SAPO-11) has good selectivity for reacting n-C16 in other decoy mixtures. While large pores (Beta, Mordenite, USY, and SDUSY) have a low activity to convert n-C16, which has to wait until i-C19 is completely converted. For this reason, it is related to limited pore size. In addition, Kim et al. (2013) revealed that when increasing the thickness of a zeolite nanosheet, the isomer yield decreased from 50% with a 2 nm thick sheet to 22% when using a 300 nm sheet. Yadav et al. (2009) said that catalytic activity is dependent on morphology, particle size, and surface area.

3. Reaction Conditions

3.1. The Effect of Temperature and Pressure

Temperature is among the most important parameters in long-chain paraffin hydroisomerization due to their high reactivity properties that can form crack products. The carbon chain isomerization can be adjusted according to the type of metal catalyst and the reaction temperature used. For lower temperatures, around 220-330 °C, noble metal catalysts can be used, while for temperatures above 300 °C, transition (non-noble) metal catalysts are used. The optimal temperature and pressure for hexadecane hydroisomerization against a Pt-loaded bifunctional catalyst typically range between 220-310 °C and 20–60 bar (Batalha et al., 2013; Du et al., 2018; Lee et al., 2014; Parmar et al., 2014; Regali et al., 2014b; Zhang et al., 2016) in fix bed reactors. In the hydroisomerization of dodecane on bifunctional catalysts loaded with Pt, the optimum temperature and pressure are 260-330 °C and 20 bar (Du et al., 2018; Liu et al., 2015; Wu et al., 2018), although the reaction has also been carried out at ambient pressure at 330 °C (Song et al., 2014). Transition metals, such as Ni_2P-SAPO-11, produce the highest yield of *ca.* 65% at temperatures of 350 °C and 20 bar (Tian et al., 2014).

Karthikeyan et al. (2016) conducted a study on the modification of zeolite β with impregnation of Pd and Ni metals for n-octane hydroisomerization with variations in the amount of metal loading, reaction temperature, and total acidity. The result showed that the conversion of n-octane increased with an increase in temperature up to 400 °C. However, the selectivity of i-octane increased up to 350 °C, after which the isomerization selectivity decreased. As the reaction temperature increased (from 350 to 450 °C), a greater amount of cracking product was formed. The increase in stable conversion at 200-400 °C might be due to the activation of the acid sites with temperature and isomerization selectivity, which was associated with the bifunctional catalysts behavior of the acid sites and metallic site in nanometer size (Karthikeyan et al., 2016). The effect of liquid hourly space velocity (LHSV), which is the ratio of liquid volume flow per hour to catalyst volume, on the yield of isomers can be seen in Table 3, in which the conversion of n-paraffin is high, but the selectivity of i-paraffin is low and vice versa (Hengsawad et al., 2018).

Table 3. The effect of LHSV in the hydroisomerization of paraffin over Pd/H- β based catalyst

Catalysts	Paraffin	LHSV (h^{-1})	T (°C)	Conversion (%)	Selectivity (%)	References
Pd /H- β	n-C_8	2	350	46.5	90.3	Karthikeyan et al., 2016
Pd-Pt/H- β	n-C_{16}	3	200	90	74	Bauer et al., 2014
Pd-Ni/H- β	n-C_8	2	350	74.9	92.4	Karthikeyan et al., 2016

Du et al. (2015) conducted a study of the effect of temperature and initial hydrogen pressure on isomerization reactions in the heavy oil slurry hydrocracking phase. Short-chain hydrocarbons were produced through the thermal cracking of the hydrocarbons supported by an increase in temperature. Meanwhile, the high reaction temperature facilitated the condensation of hydrocarbon free radicals, which increased coke formation (Wang et al., 2019). Hydrogen was easily broken down into hydrogen-free radicals at the active site of the metal dispersed catalyst (Pimerzin et al., 2019). Thus, the high concentration of hydrogen free radicals could inhibit the cracking and condensation of free radical hydrocarbons (Nguyen et al., 2020; Peraza et al., 2010). As already explained, coke could enter into the acid site of the catalyst, thereby upsetting the metal-acid site balance.

Calemma et al. (2000) reported that high pressure of hydrogen decreases the conversion of n-C16 using Pt/SiO_2-Al_2O_3 catalyst significantly, with the conversion drops from about 60% at 20 bar (290 °C) to about 30% at 80 bar (330 °C). In addition, Bauer et al. (2014) with a screening experiment conducted in a microautoclave revealed that at H_2 pressure of > 80 bar, low paraffin conversion (<10%) was obtained. To obtain a similar conversion rate between 50 bar and 1 bar H_2 pressure, the reaction temperature should be increased by about 20 °C. This shows that higher temperature is required to break the higher hydrogen pressure into ion hydrogen. In addition, at a temperature of 215 °C, an increase in pressure from 1 bar to 50 bar could reduce the hexadecane conversion value from 100% to 50%. This is due to the very low concentration of olefin intermediates at high pressure and the higher hydrogen concentration at the catalytically active site of the hydrocarbon molecules. Although higher hydrogen pressure has a negative effect on n-paraffin conversion and a lower increase in selectivity and in catalyst stability, industry specification can initiate catalyst characterization in the pressure range of 30-50 bar (Elsayed et al.,2017; Regali et al., 2014).

3.2 Contact Time

The contact time is the time spent by the reactants in order to pass through the catalyst bed during a reaction (Rahmadhaniar et al., 2020). Table 4 shows that increasing the contact time results in an increased overall conversion of n-C_7 at the constant operating condition and a decreased selectivity to hydroisomerization. In addition, with increasing contact times lead to a lower mono/multi-branched isomers ratio. It shows that the formation of multi-branched isomers slightly increases with increasing contact times. This phenomenon could be due to continuous reaction on an initial formation of mono-branched isomers into multi-branched isomers.

Table 4. Product composition and conversion from *n*-C_7 at different contact time intervals by Pt-based catalysts

Catalyst	Time interval (min)	Conversion	Selectivity	Mono/di–branched (C_7)	Reference
Pt/β	30	20	88	5.5	Wang et al., 1997
	120	70	72	3.5	
Pt/Al	30	36.78	36.4	0.29	Dhar et al., 2017
	120	58.22	58	0.26	

Contact time between reactant and active site is determined by diffusion rate and material support characteristics. Diffusion is depent on material crystallite characteristics such as crystallite size, pore apertures size, channel intersections size, and acid site density (Gnanamani et al., 2012). Having the big enough space in the vicinity of the acid site to permit the intermediates of the desired reaction to form yet small enough to limit the formation of coking intermediates by strict constraints is good choice of pore structure. In addition, the diffusion of the desirable reactant must be quick enough for the reactant transformation to be restricted to the formation of the desired product without the formation of coking (Sievers et al., 2016).

4. Conclusions

Various types of catalyst supports have produced high hydroisomerization activities, such as silica, alumina, zeolites, zirconia, and mesoporous materials. Strucure modifications that are essential to achieve a high performance hydroisomerization catalyst include increasing the acid site with suitable Lewis/Bronsted acidity, increasing the surface area with an even pore distribution, and loading the metal according to the acid site as a bifunctional catalyst. Catalysts with good hydroisomerization activity have the characteristics of high hydrogenation and low acidity, enabling them to maximize the hydroisomerization reaction compared to the cracking reaction. To increase the percent conversion and isomerization selectivity, reaction conditions such as temperature and pressure must also be adapted to the catalytic system. Temperature and contact time are among the most important parameters in long-chain paraffin hydroisomerization because a very high temperature can can cause the undesired cracking of the reaction products. Geothermal silica is an alternative source for catalyst supports suitable in hydroisomerization, however, several modification steps are still needed to obtain catalysts with good activity and selectivity.

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