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Review

Cross-metathesis of biomass to olefins: Molecular catalysis bridging the gap between fossil and bio-energy



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ABSTRACT

Terminal olefins are important building blocks for the industry of biofuels, oligomers, and lubricants production. The industrial processes for production of olefins involving oligomerization of ethylene or cracking of petrochemical waxes have several flaws including low yield and high cost in product separation. Cross-metathesis of bio-derived unsaturated fatty esters and olefins with ethylene (ethenolysis), allows the conversion of sustainable waste biomass to various renewable olefins with much safer, less toxic, sustainable, and zero-CO₂ emission processes. To our best knowledge, however, a comprehensive summary of key advances in this field (since 2017) is yet to be available, particularly on molecular features of homogeneous and heterogeneous catalysts. This paper presents a critical review on molecular structures of metal complex and oxide catalysts for ethenolysis of olefins and oleochemicals. The influence of cationic centers, coordination conditions, nature of ligands, operating conditions on catalyst performances will be systematically discussed along with relevant reaction mechanism. The key challenges for rational design of coordinated cationic hybrids have been summarized, which will provide insights to technological advancement of large-scale production of oleochemical-derived olefins.

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1. Introduction

1.1. Sustainable markets for oleochemicals

As the demand of depleting fossil fuel reserves worldwide increases in the past few decades, the costs for producing fine chemicals from petrochemicals have elevated significantly. In this context, terminal olefins are important feedstock for pharmaceuticals, biofuels, polymers and lubricants industries [1,2]. Industrially, terminal olefins can be generated by Fischer-Tropsch (F-T) and ethylene oligomerization process (Fig. 1) [3,4]. However, F-T process produces terminal olefins with low yields. Ethylene oligomerization process can only produce even-number olefins [5,6]. Another problem associated with these traditional processes is the production of a broad range of alkenes, making product purification very cost-ineffective. Alternative technology is urgently needed for producing value-added terminal olefins with high chemoselectivity in energy economical ways.

Replacing fossil fuel-based terminal olefins with bio-based oleochemicals and olefins provides greener routes to our everyday

megaton products. Oleochemicals are often byproducts or less-valued wastes from the food industry, which are not suitable for human consumption, but can be transformed into specialty products in oleochemical industry [7–9]. The global market for oleochemicals is projected to reach USD 28.6 billion by 2025 [10]. The U.S. Energy Information Administration projects renewables the most used energy source by 2050 in the International Energy Outlook 2019 (Fig. 2) [11].

More importantly, the fast expanded availability of ethylene from natural gas liquids provides a major impetus for cross-metathesis of oleochemicals as a key process for future bio-refineries. According to the GlobalData's latest report, the global ethylene capacity is projected to grow from 184 to 279 million tons per annum from 2017 to 2026 [12]. In this context, converting vegetable oils, fats and disposed oils from food industry undoubtedly generate extensive interests.

1.2. Coordinated catalytic materials

Taking oleochemicals as starting materials, cross-metathesis with ethylene, also referred as ethenolysis, is a key catalytic reaction to convert oleochemicals with internal C=C bonds into terminal olefins [13]. The rearrangement of functional groups of alkenes

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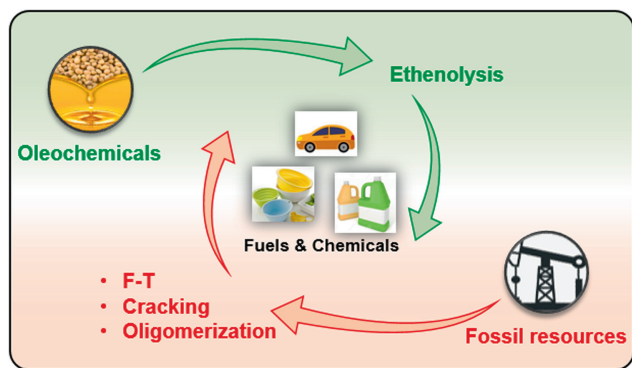


Fig. 1. Ethenolysis of oleochemicals represents a promising alternative route to replace fossil resources for manufacture of everyday commodities.

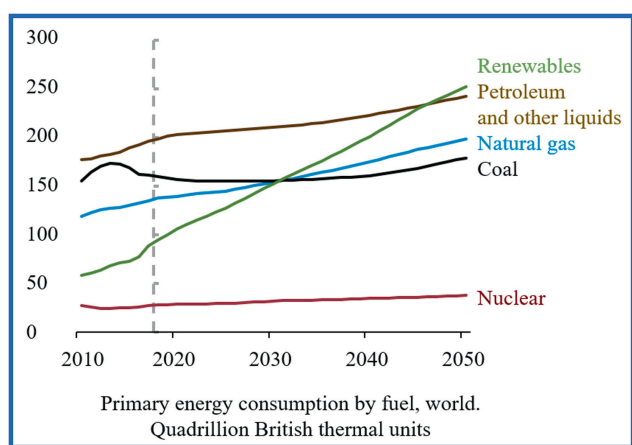


Fig. 2. International Energy Outlook 2019 projects renewables the most used energy source by 2050 [11].

occurs via cutting and reforming C=C bonds [13]. The ethenolysis chemistry contributes to global sustainability with reduced CO₂ emission and toxicity. Turner's work was among the first to recognize the utility of ethenolysis for production of terminal olefins [14]. Since then various processes have been developed to produce 1-alkenes over a wide variety of transition metal compounds [15]. Chlorides [16], alkylidene complex [17], and some transition metal oxides were among the most reported metathesis catalysts. Generally, ethenolysis can be catalyzed by chlorides (WCl₆, WOCl₄ and ReCl₅) [16], well-defined alkylidene complexes [18], and transition metal oxides (Re₂O₇/Al₂O₃, MoO₃/SiO₂, WO₃/SiO₂) [19,20]. Although considerable progress in catalyst design and synthesis of the homogeneous catalysts has been accomplished, to improve their intrinsic process ability, overall lifetime and the ease of final products separation remains a grand challenge. Hence, the development of new economically viable approaches is highly desired in this field.

1.3. Scope of this review

To our best knowledge, critical discussion on catalyst development for cross-metathesis itself is still limitedly available in literature. While general information on metathesis reactions have been summarized recently [21–23], research efforts worldwide are primarily focused on active Ru-based materials for facile metathesis reactions [2]. Several focused review articles have been published on olefin metathesis for pharmaceutical manufacturing [24], rubber industry [25], musk macrocycles production [26–28],

and terpenes upgrading [29]. While only catalyst performances for conversion of fatty acids and vegetable oils have been summarized by Karuna [30], Scott [13], Grela [31], and Bruneau [32], comprehensive discussion on catalyst design and reaction mechanism has yet to be documented in existing literature.

Hence, a comprehensive review on rational design of homogeneous and heterogeneous catalyst materials and reaction mechanism for cross-metathesis of bio-derived substrates are urgently needed, to summarize the key achievements in past four years in this area. This review paper will particularly focus on design and synthesis of active, selective, and durable Ru, Re and Mo-based homogeneous and heterogeneous catalysts for facile metathesis of two important bio-feedstocks, oleochemicals and bio-olefins. The influence of cationic centers, nature of ligands, operating conditions on catalyst performances will be discussed point-by-point along with reaction mechanism.

2. Ethenolysis of Oleochemicals over Homogeneous Catalysts

The transformation of vegetable oil through metathesis reactions in the presence of Ru-based catalyst has been industrialized by Elevance [33]. Ru-based complexes were reported to be highly active for the ethenolysis and cross-metathesis of oleochemicals and their derivatives, such as methyl oleate (MO) [34,35], ethyl oleate (EO) [36,37], fatty acid methyl esters (FAMES) [38,39], and other chemicals [40]. The main focus of this part is to illustrate the influence of catalyst structures on conversion and selectivity towards targeted product.

Ru- and Mo-based catalysts. Carbene-coordinated organometallic complexes have been the most popular choices for olefin metathesis reactions. Previous researchers have successfully synthesized a series of transition metal carbene complexes for metathesis reactions [41,42]. Carbenes are often known as strong Lewis bases, as excellent σ -donors and poor π -acceptors. Such molecular structures afford metal-carbon bonds which are usually less labile compared with metal-phosphine bonds [43]. The decreased lability of carbenes is believed to be one of the reasons for the improved thermal and oxidative stability of the corresponding organometallic complexes. Moreover, the electronic properties and the steric environment of heterocyclic carbenes can be easily and rationally altered by substituting the ligands on the carbene framework [44]. Subsequently, fine-tuning the catalytic properties of the resulting organometallic complexes can be accomplished for experimental studies.

2.1. Ethenolysis of methyl oleate

Ru-based catalysts. Ethenolysis of MO results in methyl 9-decenoate as key product as shown in Fig. 3(a), which can be applied for the production of polymers and copolymers [45]. Skowerski *et al.* [46] synthesized cyclic alkyl amino carbene (CAAC) Ru benzylidenes (Fig. 3, Ru211) and bis (CAAC) Ru indenylidene (Fig. 3, Ru212) complexes and evaluated the performance for ethenolysis of MO. Ru212 catalysts displayed high activity and initiation rate for MO due to strong steric repulsion between two CAACs. At a catalyst loading of 0.005%, Ru211 and Ru212 showed remarkable activity (TON 86,000–94,000, Table 1, #1,2). However, the synthesis method of Ru211 is more difficult than Ru212. The synthesis of Ru212 requires only six steps and is not burdened with any safety and processing issues. CAAC have led to numerous discoveries in the area of Ru olefin metathesis. A comprehensive review of the influence of CAAC ligands in metathesis reactions has been reported by Morvan's group [61]. Grubbs *et al.* [47] reported an expanded family of CAAC Ru (Fig. 3, Ru213, Ru214) catalysts and tested for ethenolysis of MO at 40 °C and 1 MPa pressure. In the

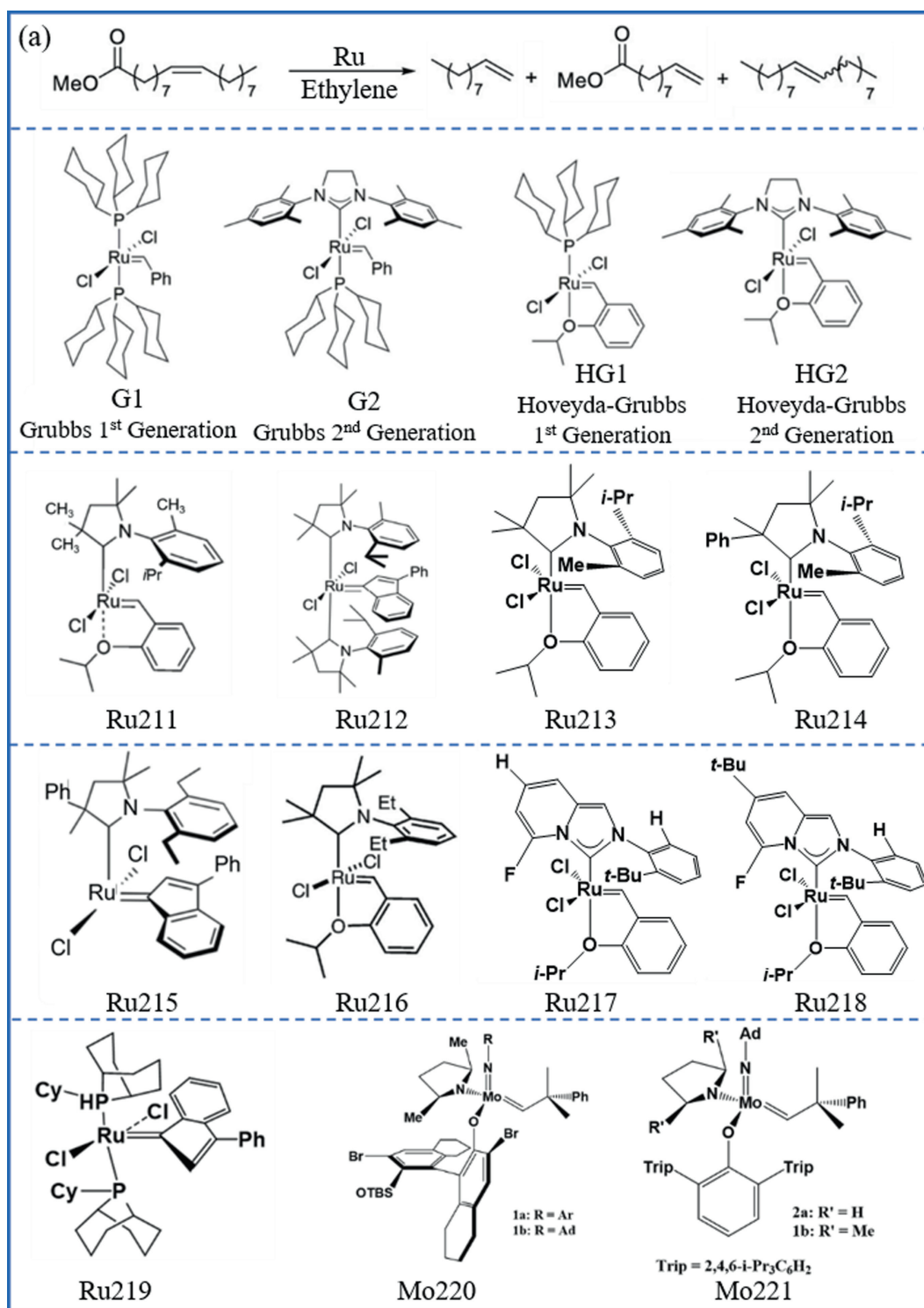


Fig. 3. (a) Ethenolysis of MO [45], Ru211 and Ru212 [46], Ru213 and Ru214 [47], Ru215 [17], Ru216 [48], Ru217 and Ru218 [49], Ru219 [50], Mo220 and Mo221 [52].

ethenolysis reaction of seed oil derivative MO, a TON value of 180,000 was achieved using only 0.003‰ loading of catalyst Ru213 and Ru214 possessing asymmetric *N*-aryl substituents. When 0.001‰ of Ru213 and high purity of ethylene were employed, a dramatically high TON of 340,000 was noted (Table 1, #3,4). It was concluded that smaller Me substituent could promote the coordination of olefin molecules on Ru active centers. On the other hand, the larger *i*Pr substituent protects the methylenide intermediate from decomposition. The asymmetry might play cru-

cial role in affecting the catalytic performances of CAAC ligated catalysts, as the conformation of the *N*-aryl ring was influenced by the steric interaction of the ortho substituent with the adjacent methyl substituent. The CAAC-ligated Ru complexes have been shown to display relatively slower reaction rates than phosphine or *N*-heterocyclic (NHC)-ligated complexes [48]. In another study, Fogg *et al.* [17] reported a fast-initiating, indenylidene complex (Fig. 3, Ru215) with good activity and scalable synthesis by CAAC and chloride donor. The steric protection at the CAAC carbon and the

Table 1
Ethenolysis of oleochemicals over Ru-based catalysts

#	Catalyst	Reaction conditions	Conversion X/%, selectivity S/%	Ref.
1	Ru211	MO, 40 °C, 1 MPa, 2 h, 0.005%	X = 51%, S = 92%, TON = 94,000	[46]
2	Ru212	MO, 40 °C, 1 MPa, 2 h, 0.005%	TON = 86,000	[46]
3	Ru213	MO, 40 °C, 1 MPa, 3 h, 0.001%	TON = 340,000	[47]
4	Ru214	MO, 40 °C, 1 MPa, 3 h, 0.003%	TON = 180,000	[47]
5	Ru215	MO, 40 °C, 1 MPa, 4 h, 0.005%	X = 48%, S = 90%, TON = 86,000	[17]
6	Ru216	MO, 40 °C, 1 MPa, 0.5 h, 0.01%	X = 42%, S = 83%, TON = 35,000	[48]
7	Ru217	MO, 60 °C, 1 MPa, 3 h, 0.1%	X = 44%, S = 79%, TON = 3400	[49]
8	Ru218	MO, 60 °C, 1 MPa, 3 h, 0.1%	X = 51%, S = 77%, TON = 3900	[49]
9	Ru219	MO, 50 °C, 1 MPa, 2 h	X = 64%, S = 97%, TON = 12,450	[50]
10	G1	MO, 50 °C, 1 MPa, 2 h	X = 43%, S = 99%, TON = 8542	[50]
11	HG/SiO ₂	MO, 40 °C, 0.03 MPa	X = 82%, S = 77%	[51]
12	Mo220	MO, 50 °C, 1 MPa, 15 h	X = 95%, S = 99%, TON = 4750	[52]
13	Ru221	EO, 50 °C, 1 MPa, 3 h, 0.5%	X = 70%, S = 90%	[44]
14	Ru222	EO, 70 °C, 2 MPa, 5 h, 0.05%	X = 89%, S = 76%	[53]
15	Ru223	EO, 70 °C, 2 MPa, 5 h, 0.05%	X = 67%, S = 97%	[53]
16	G2	EO, 60 °C, 1 MPa, 0.02%	X = 95%, S = 43%, TON = 32,018	[37]
17	Ru224	EO, 60 °C, 1 MPa, 0.02%	X = 56%, S = 75%, TON = 21,312	[37]
18	Ru225	EO, 50 °C, 1 MPa, 3 h, 0.02%	X = 18%, S = 83%, TON = 7500	[36]
19	Ru231	FAMES, 20 °C, 1 MPa	X = 99%, S = 96%	[39]
20	HG2	Canola oil, 50 °C, 1 min	X = 96%, Y = 21%	[54]
21	HG1	Cashew nutshell, 1 MPa, 12 h	Y = 84%	[55]
22	HG1	Cardanol, RT, 1 MPa, DCM, 24 h	Y = 96%	[56]
23	HG1	Algae oil, 1 MPa, CO ₂ , 45 °C, 18 h	X = 90%, S = 97%	[57]
24	Ru232	Cocoa butter, RT, 0.1 MPa, 2 h	X = 30%	[58]
25	Ru233	Cardanol, 60 °C, 0.3 MPa	X = 63%, S = 89%, TON = 630	[59]
26	Ru234	Cardanol, 60 °C, 0.3 MPa	X = 33%, S = 79%, TON = 330	[59]
27	Ru235	Styrene, 35 °C, DCM, 5 h	X = 99%, S = 100%	[60]

Note: Ru233, Ru234 and Ru 235 are Ru complexes immobilizing on Si supports. Conversion = 1 – (final moles of reactants)/(initial moles of reactants) × 100%; Selectivity = (moles of ethenolysis products)/(moles of ethenolysis products + cross-metathesis products + self-metathesis products) × 100% (note: the stoichiometric numbers should be consider for different substrates); TON = mols of ethenolysis product/mols of catalyst.

volatility of the bridging chloride donor makes the reactivity of Ru215 (Table 1, #5) improved [17]. Optimal TON was obtained at 1.4 MPa of ethylene pressure indicating a balance between ethylene solubility and catalyst poisons. They also studied the initiation rate in ethenolysis of MO with *tert*-butyl vinyl ether. It was observed that the incorporation of a labile dative ligand reduces the barrier to initiate the indenylidene, which is even comparable to the benzylidene ligand. The Ru-based metathesis catalysts bearing CAAC ligands were also found to exhibit an good performance in converting the seed-oil derivative MO by ethenolysis reaction (TON 35,000) with a catalyst loading of 0.01% (Fig. 3, Ru216, Table 1, #6) [48]. Except for the Ru-based catalysts with five-membered CAAC ligands mentioned above, Ru-based catalysts with more π -accepting and σ -donating six-membered CAAC ligands were synthesized and tested for MO ethenolysis reaction [52]. However, these catalysts displayed much lower TON (<2000) at 40 °C for MO ethenolysis reaction comparing to the catalysts with five-membered CAAC ligands.

Hong *et al.* [49] developed a family of Ru-based catalysts bearing fluorinated imidazo [1,5- α] pyridine-3-ylidene carbenes (F-ImPy, Fig. 3, Ru217, Ru218). The presence of a monoortho-substituted *N*-aryl group enhanced the activity of Ru217. They found Ru218 showed even higher TON than Ru217 catalyst due to the existence of σ -donating *t*-Bu group on the backbone (Table 1, #7,8). As the pressure of ethylene increased, the selectivity increased due to higher solubility in MO. At higher temperature, the TON has negligible changes, but the selectivity is slightly lower. Ru218 catalyst formed highly stable Ru intermediate at high temperature, thus showed higher selectivity and stability under ethylene atmosphere and ambient temperature (moisture and air) without catalyst decomposition (up to 100 °C). For the ethenolysis reactions, the low stability of the most o first- and second-generation Ru-based catalysts is mainly due to the involve of methylidene intermediates which tends to deactivate through bimolecular coupling and metal reduction [63–66]. Thus glovebox

and ethylene with ultrahigh purity are desired for high activity. The F-Ru interaction can improve the stability of the Ru catalyst. The substituents at the C5 position have significant effect to improve the stability of the Ru complex [67,68]. Ru complexes were reported with high stability at high temperature under ethylene atmosphere due to the nature of *N*-alkyl substitution, e.g. high steric bulkiness [36]. Winde's group [50] compared G1 and Ru-alkylidene complex (Ru219) with ethenolysis of MO at 50 °C and 1 MPa. The X-ray crystal structure of Ru219 indicated the presence of an indenylidene moiety and cyclohexylphoban ligands (Cy, Fig. 3) and displayed improved stability to air and moisture than G1 catalyst for MO ethenolysis reaction. They demonstrated that combination of phosphorus containing ligands with a Ru-indenylidene moiety gave significantly higher TON of 12,450 at the end of run compared to TON of 8542 of G1 (Table 1, #9,10) [50]. Two years later, much higher TON (22,000) of ethenolysis of MO was reported on G2 catalysts with 22% yield of 1-decene (only 0.01% metal loading) [69].

Immobilization of homogeneous catalysts in ionic liquids (ILs) has also been studied [70]. Apesteguia *et al.* [51] supported a HG2 complex on silica (HG2/SiO₂) for ethenolysis of MO (Table 1, #11). The infrared spectroscopy (IR) and diffuse reflection using Fourier transform spectroscopy (DRIFTS) confirmed the structure of the HG was well retained after immobilization. They compared the performances of free HG2 complex and the immobilized one. The results showed that the HG2 complex loses some activity for MO ethenolysis when it was supported on silica. ICP results showed that there is no detectable Ru in the liquid phase after reaction. Hence, the catalytic activity is solely from the immobilized HG2/SiO₂ catalyst. The pressure effect indicated catalyst deactivation due to the inhibition of the metathesis cycle at higher ethylene pressure. As the reaction temperature increased, the yield decreased. It was also noticed that as the ratio of ethylene to MO increases, MO yield increased due to the equilibrium shift and the suppression of the competitive MO self-metathesis reaction.

Mo-based catalysts. The use of inexpensive Mo oxo species for the ethenolysis of renewable biomass-based feedstock to produce fine chemicals is a low cost and an easy synthetic process. Robust, cheap, and recyclable heterogeneous catalysts are more desirable for an industrial process. Mo-based monoaryloxide-pyrrolide (MAP, Fig. 3, Mo220, Mo221) [52] were prepared through addition of a phenol to a bispyrrolide and reported for MO ethenolysis at room temperature and relatively ethylene pressure of 1 MPa with high performance towards 1-decene ($X = 95\%$, $S > 99\%$, TON 4750, Table 1, #12). MAP species have high stability under ethylene atmosphere due to the presence of stable methyldiene species. But the oxophilic and sensitive nature of transition Mo metal, as well as a low solubility of ethylene in MO were the major limiting factors that hinder high conversion [52]. Taoufik *et al.* reported the ethenolysis of MO over $\text{MoO}(\text{CH}_2\text{CMe}_3)_3/\text{SiO}_2$ catalyst, which was obtained by grafting the $\text{MoOCH}_2\text{CMe}_3)_3\text{Cl}$ precursor onto a silica support and displayed a TON of 5000 after 15 h [71].

2.2. Ethenolysis of ethyl oleate

The ethenolysis of EO is targeted to produce ethyl dec-9-enoate and dec-1-ene, with undesired byproducts of diethyl octadec-9-enedioate and octadec-9-ene that obtained in the self- and cross-metathesis reaction (Fig. 4(a)) [72]. Grela *et al.* [44] screened 65 different Ru complexes for conversion of EO without using glovebox, protective atmosphere, or ethylene with ultrahigh purity to obtain highly active catalyst under practical and industrial condi-

tions. A catalyst bearing the unsymmetrical NHC featuring a thiophene fragment (Ru221, Fig. 4(b)) gave the best activity and selectivity at 1 L scale of reaction with a 90% pure substrate (Table 1, #13). The results showed that the symmetrical NHC-based complexes gave more self-metathesis products than G1 complexes. They found the replacement of chlorine with iodine could improve the selectivity in all cases. This result is consistent with the work reported by Hong [69]. Grela's group also tried to convert undistilled EO with grade 3 ethylene using Ru-based catalysts bearing CAAC ligand. At 50 °C, a TON of 12,900 was obtained without using a glovebox [73]. Grela *et al.* [53] synthesized various of Hoveyda-type catalysts with variation of the unsymmetrical NHC ligands (Fig. 4(b), Ru222). They compared the performance of Ru223 (Fig. 4(b)) bearing CAAC type ligand and Ru222. Results showed that Ru222 were less active than CAAC complex Ru223 (Table 1, #14,15). As the temperature increased, the catalytic activity of Ru223 decreased, while the selectivity dropped. However, the Ru222 bearing NHC ligands were still stable at higher temperature.

Togni *et al.* [37] reported the synthesis of Ru metathesis catalysts and noticed that *N*-trifluoromethyl catalysts (Fig. 4(b), Ru224) displayed high selectivity to terminal olefins in the ethenolysis reaction (Table 1, #16,17) ascribing to the electronically unsymmetrical nature of the *N*-trifluoromethyl. It explained the decreased selectivity when *N*-trifluoromethyl was replaced with a sterically equivalent *N*-iPr. These results confirmed the important role of electronic bias imposed on the NHC ligand by

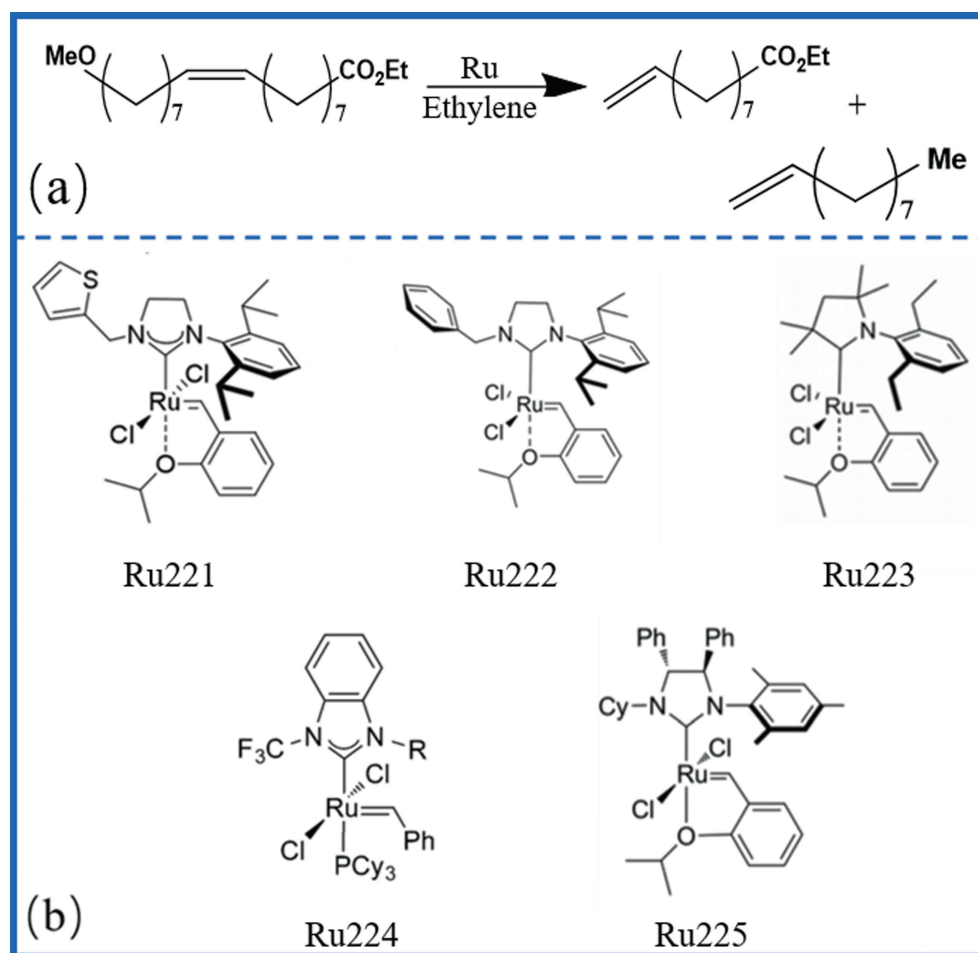


Fig. 4. (a) Ethenolysis of EO [44], (b) Ru-based catalysts for ethenolysis of EO, Ru221 [44], Ru222 and Ru223 [53], Ru224 ($R = 3,5\text{-CF}_3\text{Ph}$) [37], Ru225 ($R = \text{CH}_3$ or $R = \text{CH}_3\text{CHCH}_3$) [36].

the strong Ru-F interaction, and electron withdrawing for tuning the catalytic performance in ethenolysis reaction. Catalyst Ru224 outperformed catalyst G2 when using 0.1% Ru loading. However, the catalytic performance of Ru224 reduced dramatically at 0.02% catalyst loading while G2 maintained its high activity (TON 32,018) and good durability. Grisi *et al.* [36] synthesized new Ru-based catalyst bearing unsymmetrical NHC ligand (Fig. 4 (b), Ru225, Table 1, #18). The nature of *N*-alkyl substitution and the higher steric bulkiness accounts for the observed higher stability. This work further confirmed the import influence of the type and structure of the NHC substitution pattern on the reactivity for ethenolysis reaction.

2.3. Ethenolysis of triglycerides and cardanol

Bio-feedstock and bio-waste are viewed as an important inexpensive feedstock for FAMES [58]. In 1995, $\text{WCl}_6/\text{Me}_4\text{Sn}$ was investigated for the ethenolysis of palm oil (oleic, linoleic, and palmitic acids) with ethylene at 30 °C and 0.1 MPa in dry chlorobenzene. A yield of 18.9% 1-decene was obtained [74]. Klaas's group converted the fatty acid esters from high oleic sunflower oil using heterogeneous $\text{Re}_2\text{O}_7/\text{SnBu}_4$ catalysts under at 20 °C and 5 MPa with 1-decene yield of 20% [75]. In addition, $\text{Re}_2\text{O}_7\text{-B}_2\text{O}_3/\text{Al}_2\text{O}_3\text{-SiO}_2/\text{SnBu}_4$ catalyzed ethenolysis of the meadow foam oil methyl ester at 20 °C and 4 MPa. 77% conversion, 94% selectivity and 154 TON towards 1-decene were observed in 3 h [76]. In this section, an overview of triglycerides ethenolysis literature including performances of homogeneous and heterogeneous catalysts, as well as the preliminary understanding on catalytic active sites based on surface characterization will be presented along with a brief summary of unsolved issues with existing technologies.

Ru-based catalysts are still the most widely studied for FAME (61% MO, 21% methyl linoleate, 8% methyl linolenate) ethenolysis reactions [73]. Sehitoğlu *et al.* [39] prepared homobimetallic Ru

alkylidene complexes for the ethenolysis of rapeseed oil-derived FAMES at 25 °C and 0.1 MPa ethylene pressure (Ru231, Fig. 5(a)). The homobimetallic complexes are more active ($X = 99\%$, $S = 96\%$) than their monometallic analogs with less isomerization products formed (Table 1, #19). Arshad *et al.* [54] reported a microwave-assistant ethenolysis of canola oil derived methyl esters (TOF 26,000 min^{-1} , Table 1, #20) and canola oil (TOF 10,300 min^{-1}) using HG2 catalyst. The impurities in the canola oil led to a lower TOF for ethenolysis reaction comparing to the canola oil derived FAMES. Ullah *et al.* [77] reported solvent-free and atom-efficient ethenolysis of canola oil ($Y = 45\%$, TON 21,820), chicken fat ($Y = 45.7\%$, TON 78,080) and waste cooking oil ($Y = 71\%$, TON 92,000) esters at low temperature using G2 and HG2 catalysts and microwave method. In this process, no purification of the esters and no organic solvent are needed. They observed that the catalyst was consumed towards isomerization of reactants, thus lead to a low selectivity to the desired products. This work provided a rapid and green approach to obtain efficient catalysts for converting waste lipidic resources to useful bio-based polymer precursors.

Goossen's team reported cashew nutshell liquid (CNSL, 60%–70% anacardic acid, 10%–20% cardol, 3%–10% cardanol, Fig. 5(b)) ethenolysis reaction over HG1 catalyst [55]. The cheap and non-edible CNSL is abundant available with a production of 1.2 million tons per year [55]. This catalyst converted CNSL with high yield ($Y = 84\%$) using dichloromethane (DCM) as the solvent at room temperature and 1 MPa (Fig. 5(c), Table 1, #21). No turnover was observed if DCM was replaced by other greener solvent. Cole-Hamilton *et al.* [56] synthesized 3-vinylphenol from cardanol by ethenolysis and isomerization reaction. The Ru-based HG1 catalyst displayed higher performance ($Y = 96\%$, Table 1, #22) than G1 ($Y = 85\%$) and HG2 ($Y = 11\%$) for the ethenolysis of cardanol using anhydrous DCM as solvent. Mecking's group proposed a straightforward approach of combined extraction and catalytic functional-

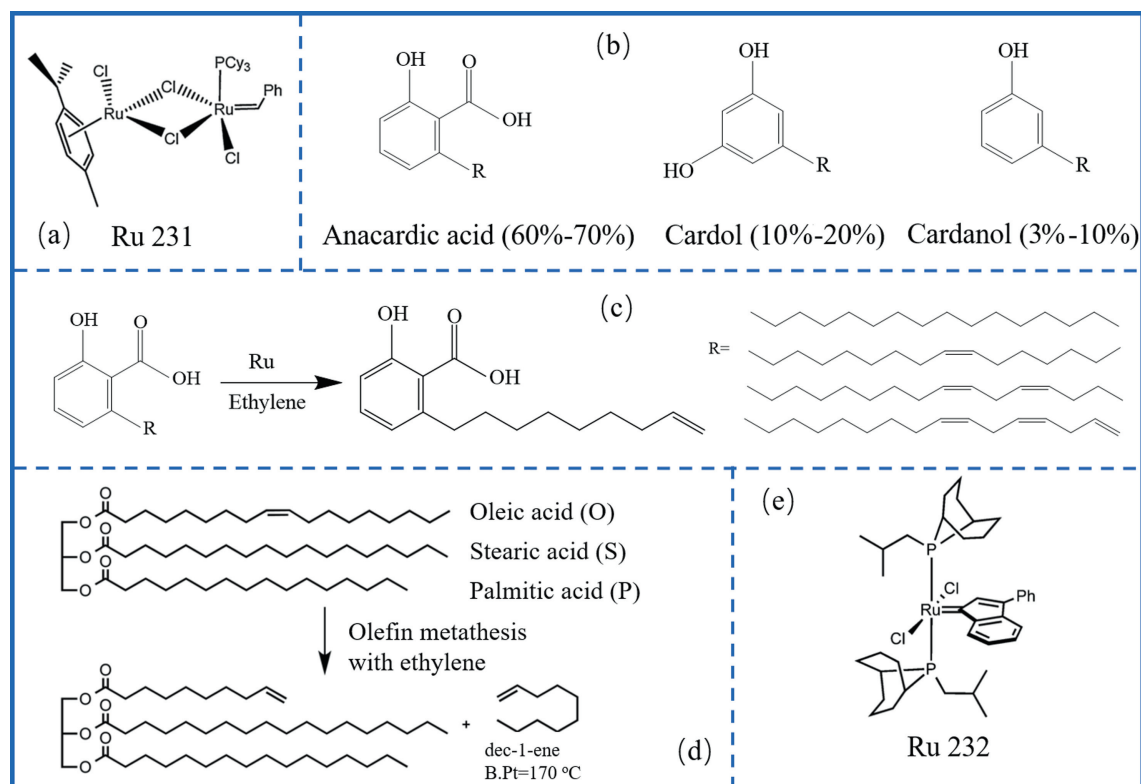


Fig. 5. (a) Ru231 [39], (b) composition of CNSL [55], (c) the conversion of CNSL over metathesis reaction [55], (d) ethenolysis of cocoa butter triglycerides [78], (e) Ru232 [58].

ization via ethenolysis in supercritical CO₂ [57]. The ethenolysis of the unsaturated fatty acid (18:1) in the algae oil proceeded with conversion of 90% and high selectivity of 97% with 1 MPa ethylene and 30 MPa CO₂ at 45 °C over HG1 catalysts (Table 1, #23). Furthermore, supercritical CO₂ is benign and easy to release from the final products.

One of the most unique natural oils, cocoa butter, is the only solid vegetable triglyceride. The distinct melting characteristic is attributed to its unique triglyceride compositions including 23%–31% distearoyl-oleoyl-glycerol (SOS), 18%–23% dipalmitoyl-oleoyl-glycerol (POP), 36%–41% palmitoyl-oleoyl-stearoyl glycerol (POS) (Fig. 5(d)) [78]. The typical fatty acid composition of SOS, POP and POS is oleic acid (34.5%), palmitic acid (26.0%) and stearic acid (34.5%). Transformations of cocoa butter by reaction of the carbon-carbon double bond in the alkyl chain of triglycerides, such as epoxidation, metathesis, ozonolysis, and dimerization, can potentially produce a variety of important industrially relevant intermediates. Lapkin's group reported a direct conversion of cocoa butter triglycerides obtained from waste food materials to 1-decene by ethenolysis reaction over Ru-based catalysts [58]. Electron-donating bisphosphine methylidene Ru complex (Fig. 5(e), Ru232) gave the best results for this reaction ($X = 30\%$, Table 1, #24) due to good stability of methylidene complex. At a pressure of 0.6 MPa, the conversion of the triglycerides reached the maximum. The catalytic performance has no significant change in at least 140 min.

Challenges. Although modern homogeneous metathesis Ru catalysts exhibit high activity and selectivity, which can be further tuned by proper ligand selection, their large-scale applications seem to be limited due to high cost and difficulty in separation. It is clear that several challenges still remain for future industrial development: (a) Low activity and selectivity due to C=C bond isomerization and self-metathesis of substrates and products [79]. (b) Inhibition of active sites and poor durability resulting from complexation of functional groups with catalytic active intermediates and strong interaction between by-products and active metal centers [80]. (c) High cost and difficulty in separation which includes the separation of catalyst residues from the reaction products. (d) Immobilization of homogeneous catalysts undoubtedly has great potentials in solving these issues [81]. However, limited improvement in recyclability in these systems still remain unsolved.

3. Ethenolysis of Oleochemicals over Heterogeneous Catalysts

Considering the high costs but poor performances of homogeneous catalysts, the benefits of developing novel cost effective active heterogeneous catalysts are strongly desired [82,83]. It was previously reported that metal incorporated mesoporous catalysts showed a superior catalytic performance for olefin metathesis [84,85]. The mesoporous catalysts have following advantages: (1) Easy access to active sites due to large specific surface area. (2) Narrow pore size distribution, well-ordered mesoporous structure, and controllable pore size for selective ethenolysis reactions. (3) High dispersion of active metal active centers exposed to reaction medium. (4) Tunable surface chemistry of mesoporous supports can be achieved to enhance electron withdrawing/contributing abilities. These changes will activate metal centers by polarizing metal-carbon bonding, which would selectively promote ethenolysis over other side reactions. (5) Easily managed synthesis, separation, and regeneration.

Coordinated metal incorporated heterogeneous catalysts appear to be a classic topic in the field. Actually, the concept of strong metal support interaction and single sited catalysts have been well defined in this area (Fig. 6(a)) [86]. The dispersion of active sites has always been the main challenge in the area of

heterogeneous catalysis. To address this issue, extensive fundamental research on organometallic chemistry has been performed to obtain better molecular insights [87]. A general methodology to control the nature of active sites the immobilization of metal complexes followed by activation under reductive atmosphere. Thus, the valence state of W, Mo, Ta, Re centers can be precisely tuned for activation of C=C bond.

Re₂O₇/Al₂O₃/SnMe₄ and Re₂O₇/SiO₂/Al₂O₃ were investigated for ethenolysis of MO at 25 °C and 3 MPa [88,89]. Conversion of 54% and 29% of MO were obtained with these catalysts respectively with TON of <200 after 0.5 h. It was observed that Re₂O₇/SiO₂/Al₂O₃ catalysts showed a slightly lower activity due to the stronger interaction of the ester group with the Si-Al support [90]. Re₂O₇/SiO₂-Al₂O₃/SnBu₄ catalysts with 6% B₂O₃ addition displayed a conversion of 64% and TON of 112 for ethenolysis of MO within 30 min at 50 °C and 3 MPa of ethylene pressure. Moreover, this catalyst can be recycled at least five times with negligible loss of activity [88]. In another study, an ester mixture (methyl linoleate/MO) was metathesized in the presence of Re₂O₇/SiO₂-Al₂O₃/SnBu₄ catalyst at 20 °C. Conversion of 85.6% and 47.6% were achieved for methyl linoleate and MO respectively. The selectivity towards primary metathesis product 1-decene was more than 95% [89]. Hwang *et al.* [91] grafted methyltrioxorhenium on the mesoporous ZnAl₂O₄ evaluated by the MO ethenolysis without using chloride promoter ($X = 89\%$, TON 11.2). The MO conversion was closely related to the Re loading and reaction temperature.

Heterogeneous metal incorporated mesoporous catalysts can be recycled by filtration after ethenolysis reaction. Recycled catalysts will be calcined for regeneration to remove the byproducts adsorbed on the active sites. These advantages provide strong impetus for us to investigate immobilized Ru-based catalysts or metal-based mesoporous catalysts for ethenolysis of triglycerides. G2 and HG type Zhan catalysts (ZC, Fig. 6(b)) were anchored on SBA-15 by phosphine linkers and non-covalent interaction, respectively [59]. Both ZC/SBA-15 (Ru233, Table 1, #25, TON 630) and G2/SBA-15 (Ru234, Table 1, #26, TON 330) hybrid catalysts displayed good performance in cardanol ethenolysis at 60 °C and 0.3 MPa. ZC/SBA-15 was more active compared to G2/SBA-15. However, only 0.5% Ru leaching was detected for G2/SBA-15 which is lower than 2.5% for ZC/SBA-15 catalyst. Similarly, Ru-based catalysts bearing a polar quaternary ammonium group in NHC ligand were immobilized on SBA-15 and MCM-41 to catalyze the cross-metathesis of methyl undecenate and methyl acrylate ($X = 98\%$, TON 392) at 80 °C [92]. HG2 catalyst was encapsulated within the yolk-shell structured silica (Fig. 6(c), Ru235, Table 1, #27) and displayed good performance ($X = 99\%$) in the cross-metathesis of styrene ascribing to the mesoporous structure of the shell and the hollow structure of the interior [60]. The immobilized catalysts can be reused at least eight cycles without significant activity loss.

4. Cross-Metathesis of Olefins with Ethylene

Light olefins, commonly used petrochemicals, are traditionally produced from shale gas feedstocks. In light of bridging the future gaps in the supply of commodity chemicals from biomass, butene can be produced from bio-derived γ -valerolactone from agricultural waste as a sustainable process [93]. Propene is an important feedstock for production of many petrochemicals and oleochemical, such as propylene oxide, acrylonitrile and polypropylene. Conventional, propene was produced by high temperature/pressure stream cracking method. Propene can be also obtained from propane dehydrogenation and olefin metathesis. Olefin metathesis methods can produce propene on milder conditions with less environmental contamination, hence this method is more energy efficient and cost-effective [94]. WO₃ is most widely used in the

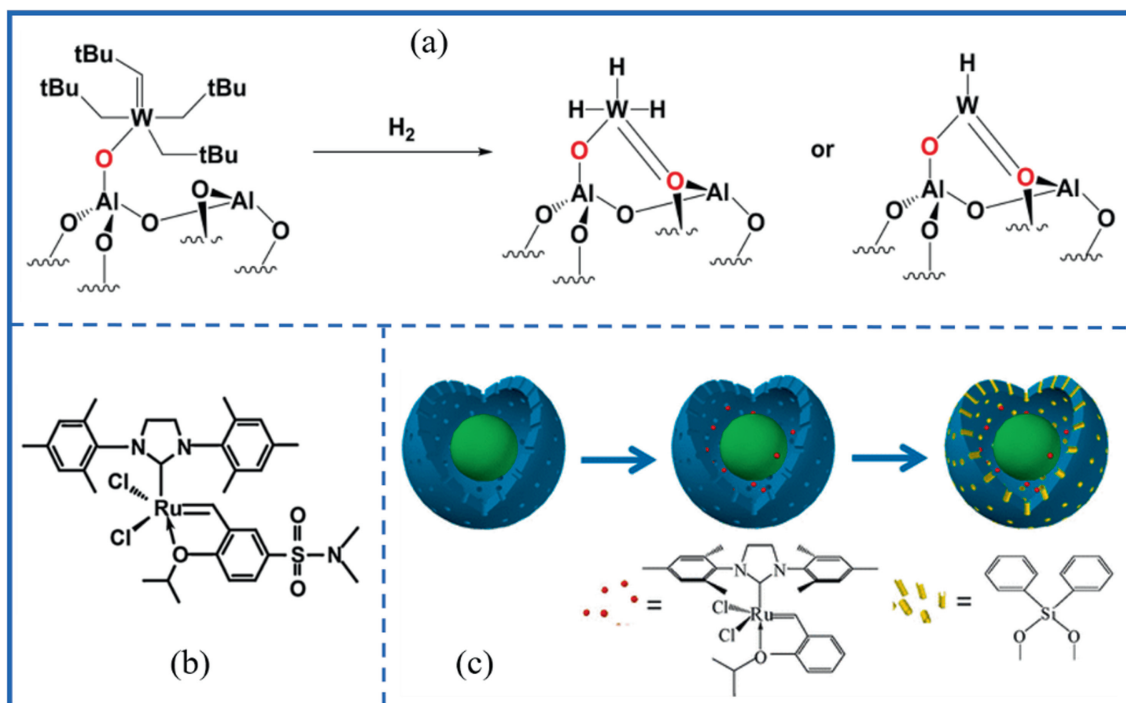


Fig. 6. (a) Structural evolution of W complexes into single sited W oxides with tunable valence states [86], (b) ZC catalyst [59], (c) encapsulating Ru235 within a yolk-shell structured silica [60].

metathesis reaction of butene and ethylene to get propene ($>280\text{ }^{\circ}\text{C}$ and $3.0\text{--}3.5\text{ MPa}$ pressure) due to the high resistance to deactivation, low price and easy regeneration. WO_3 can be deposited on various supports using different methods to obtain stable catalysts under harsh conditions. In the following part, the various catalysts, especially WO_3 , for metathesis of butene with ethylene and some other olefins will be discussed in detail.

4.1. W-based catalysts

$\text{WO}_3/\text{SiO}_2 + \text{MgO}$ catalysts. WO_3/SiO_2 catalysts are widely applied as commercial catalyst for producing propylene by olefin metathesis method due to the low price, good anti-poisoning abil-

ity, high stability, as well as easy separation and regeneration [16]. If 1-butene was selected to react with ethylene to produce propene, 1-butene was isomerized to form 2-butene in the first step in the presence of MgO as the promoter in industrial processes (Fig. 7) [95]. Zhou *et al.* [96] impregnated SiO_2 by ammonium metatungstate to obtain WO_3/SiO_2 catalyst and studied the effect of pretreatment gases (air, N_2 , N_2/H_2 , H_2) on the catalytic activity in the ethenolysis of 1-butene to propene. The formation of tetragonal WO_3 species was confirmed by the transmission electron microscope (TEM) images (Fig. 8(a), (c)). The catalyst evaluation results showed that N_2 and H_2 pretreated WO_3/SiO_2 containing both W^{6+} and W^{5+} species displayed excellent performance ($X = 86\%$, $S = 92\%$, Table 2, #1,2), whereas the air-pretreated

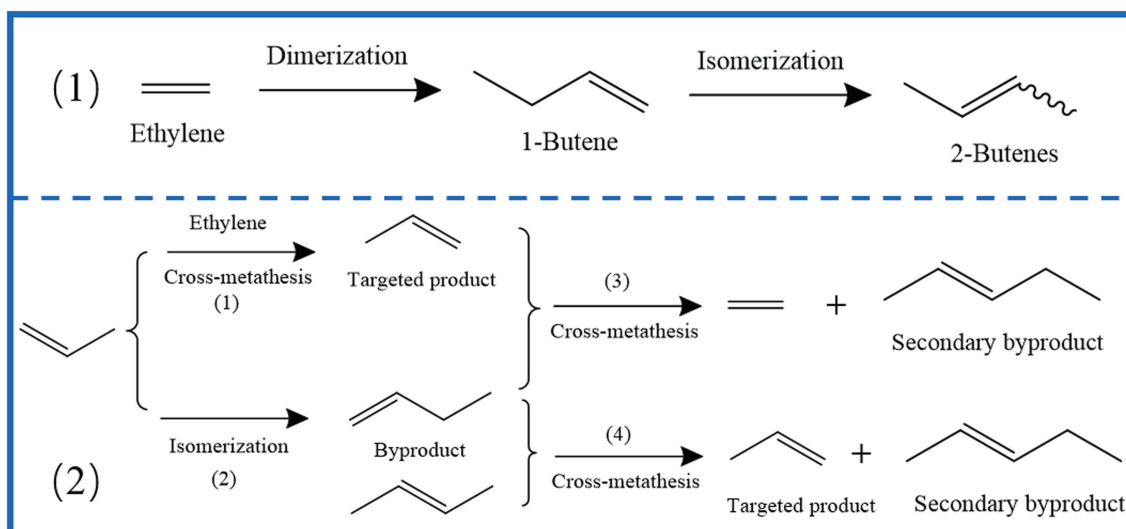


Fig. 7. Overall reaction network of converting 1-butene to propene [95].

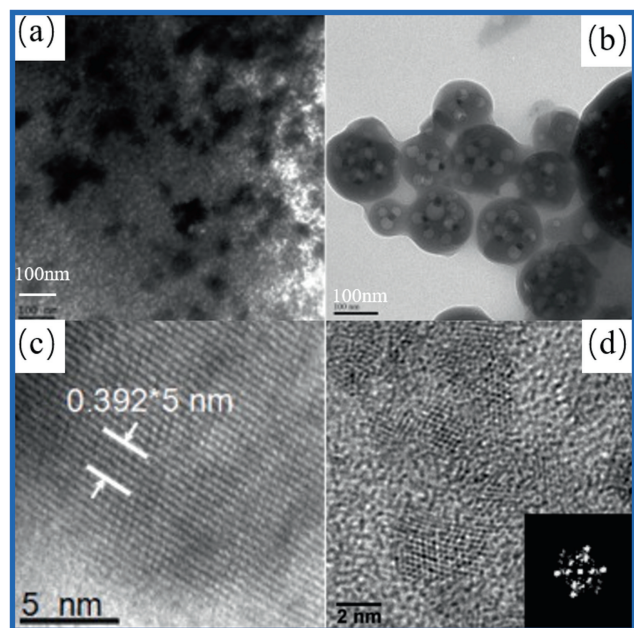


Fig. 8. TEM images of (a) $\text{WO}_3/\text{SiO}_2\text{-H/N}$ [96], and (b) WO_3/SiO_2 [99], HRTEM images of (c) $\text{WO}_3/\text{SiO}_2\text{-H/N}$ [96], and (d) WO_3/SiO_2 (2D-FFT insets) [100].

WO_3/SiO_2 are inactive which solely contained the monoclinic W^{6+} species. Hence, they concluded that the tetragonal WO_3 and partially reduced species are the active sites, whereas monoclinic WO_3 was inactive. Fourier transform infrared spectrometer (FTIR) and thermogravimetric analysis (TGA) results of the used catalysts showed that the organic compounds deposition caused the catalyst deactivation [96]. Furthermore, they observed that the presence of MgO enhanced the catalytic activity by converting 1-butene to 2-butene. In order to understand the role of MgO in the ethenolysis reaction, Chen *et al.* [97] explored the effect of MgO on WO_3/SiO_2 catalyzed 1-butene/2-butene metathesis reaction. They noticed that MgO improved the self-metathesis of 1-butene significantly (Table 2, #3,4). However, the metathesis of *trans*-2-butene and *cis*-2-butene did not show a significant enhancement [97].

To understand if the synergistic effect existed between WO_3 and MgO, Zhou *et al.* [98] synthesized several kinds of bimetallic Mg-W oxides and tested for metathesis reaction of 2-butene with ethylene. WO_3/MgO (using MgO as support) had lowest ethenolysis activity due to the lack of active WO_x species and the isomerization ability of the basic sites on MgO. $\text{MgO-WO}_3/\text{SiO}_2$ showed better activity due to the existence of active tetrahedral W species as confirmed by X-ray diffraction (XRD) and Raman spectrum. $\text{MgO}/\text{WO}_3/\text{SiO}_2$ (impregnating MgO on WO_3/SiO_2) catalysts showed higher propene yield than $\text{WO}_3/\text{MgO}/\text{SiO}_2$ and $\text{MgO-WO}_3/\text{SiO}_2$ catalysts (Table 2, #5–8). The addition of MgO increased the Lewis acid sites and improved the metathesis activity. However, in the case of metathesis of 2-butene, MgO hardly affects the propene yield. MgO can only affect the isomerization between 1-butene and 2-butene [98]. Handzlik's group investigated the stability of Mo and W oxide species on partly dehydroxylated silica by DFT calculation [111]. They found that the dioxo W(VI) species are apparently less stable than the monooxo W(VI) species. The monooxo W(VI) species are more stable than the monooxo Mo(VI) and Cr species.

WO_3/SiO_2 catalysts. Debecker *et al.* [99] prepared super-microporous WO_3/SiO_2 catalyst with no crystallites formed by one-pot aerosol assisted sol–gel process. The catalyst was highly effective for metathesis of *trans*-2-butene with ethylene to propene due to the high specific surface area, good W dispersion, micropores

structure (2 nm), perfect spherical shape (Fig. 8(b)), appropriate reducibility and surface acidity. The increasing of calcination temperature and W loading can enhance the catalytic activity in some range (Table 2, #9,10). Furthermore, the aerosol method outperformed markedly reference impregnated method due to better WO_3 dispersion (Table 2, #11) [99]. Praserttham *et al.* [100] prepared WO_3/SiO_2 catalyst by incipient wetness impregnation method and evaluated for *trans*-2-butene metathesis reaction ($X = 60\%$, $S = 49\%$, Table 2, #12). TEM and high-resolution transmission electron microscope (HRTEM) images showed the formation of small WO_x nanoparticles and the orthorhombic WO_3 crystallites (Fig. 8(d)). They found the W dispersion on the catalyst has a major effect on the coke formation and the stability of the catalysts. Low heating rate calcination is good for obtaining better dispersion of W species.

Pretreated WO_3/SiO_2 catalyst was prepared by a wetness impregnation method by Assabumrungrat's group [101]. The effect of pretreatment and calcination methods on the catalytic activity and the lifetime was studied in the metathesis of 2-butene with ethylene ($X = 75\%$, $S = 92\%$, Table 2, #13,14). Pure H_2 pretreated non-calcined catalysts displayed higher performance than the calcined WO_3/SiO_2 . The elevated temperature for H_2 pretreatment improved the activity and stability of the catalysts. Furthermore, they observed that the catalyst with optimum amount of acid sites and the total acidity exhibited highest stability during the metathesis reaction. The crystalline WO_3 may catalyze isomerization reactions and lead to the deactivation of the catalysts. The characterization results confirmed that the well-dispersed tetrahedral $\text{WO}_{2.83}/\text{WO}_2$ species favors the good catalytic performance. Furthermore, they studied the effect of the acid sites and found that the metathesis of 2-butene and the isomerization of 1-butene to isobutene increased as the Brønsted acid sites increased, whereas the Lewis acid sites drive the 1-butene isomerization to produce 2-butene [101].

In order to investigate the initiation of the olefins metathesis over WO_3 catalyst, Lo *et al.* [94] carried out density functional theory (DFT) study of the *trans*-2-butene metathesis reaction mechanism over WO_3 slabs. Both $\text{W} = \text{CHCH}_3$ sites and $\text{W} = \text{CH}_2$ sites were considered. WO_3 (001) surface with $\text{W} = \text{CHCH}_3$ active sites has five types of surface atoms as shown in Fig. 9. They found $\text{W} = \text{CHCH}_3$ sites are the initial state of the propagation process and more active than the $\text{W} = \text{CH}_2$ sites [94].

W-SBA catalysts. Hexagonal SBA-15 (6–11 nm) with large surface area, high pore volume, and narrow pore size distribution is one of the most frequently used materials for sorption and catalysis [112,113]. Al-Khattaf's group supported Mo and W species on SBA-15 and tested for the metathesis of 2-pentene. The conversion of 2-pentene is much higher in the presence of $\text{WO}_3/\text{SBA-15}$ ($X = 55\%$) than that of $\text{MoO}_2(\text{acac})_2/\text{SBA-15}$ ($X = 42\%$) and $\text{MoO}_3/\text{SBA-15}$ ($X = 40\%$) [112]. Liu *et al.* [102] supported W on various of supports (SBA-15, SiO_2 , Al_2O_3 and TiO_2) by incipient wetness impregnation method. $\text{WO}_3\text{-SBA-15}$ showed the best activity ($X = 88\%$, $S = 69\%$, Table 2, #15) towards 1-butene metathesis with ethylene due to more acid sites and higher W dispersion on larger surface area. Besides, the characterization results showed that more $\text{W}=\text{O}$ formed in isolated tetrahedral structure of surface WO_x . The reaction mechanism over W-SAB-15 catalyst was shown in Fig. 10: 1-butene was isomerized to 2-butene followed by the carbene species formation and the metathesis reaction between 2-butene and ethylene [114]. The metallocycle intermediates formation is the rate-determining steps in the olefin metathesis process. The silanol Si-OH group acted as a weak Brønsted acid site and only took part in the isomerization of 1-butene. The isolated tetrahedral W^{6+} species was reduced by olefin or H_2 to form W^{5+} species from which the $\text{W}=\text{O}$ (LAS) or W-OH (BAS) bonds then formed W-carbene species ($\text{W} = \text{CHCH}_3$). They also found that

Table 2
Metathesis of butene and other olefins with ethylene

No.	Catalyst	Reaction conditions	Activity, selectivity	Ref
1	WO ₃ /SiO ₂ -H/N	1-Butene, 280 °C, 3 MPa, 0.52 L·min ⁻¹ , 19 g, 2 h	X = 65%, S = 78%	[96]
2	WO ₃ /SiO ₂ -H/N + MgO	1-Butene, 280 °C, 3 MPa, 19 g, 2 h	X = 86%, S = 92%	[96]
3	WO ₃ /SiO ₂ + MgO	2-Butene, 300 °C, 2 MPa, 4 h ⁻¹ , 2 g, 20 h	X = 86%, S = 90%	[97]
4	WO ₃ /SiO ₂	2-Butene, 300 °C, 2 MPa, 4 h ⁻¹ , 2 g, 20 h	X = 88%, S = 90%	[97]
5	WO ₃ /MgO	2-Butene, 300 °C, 2 MPa, 4 h ⁻¹ , 2 g	X = 70%, S = 10%	[98]
6	MgO-WO ₃ /SiO ₂	2-Butene, 300 °C, 2 MPa, 4 h ⁻¹ , 2 g	X = 55%, S = 68%	[98]
7	MgO/WO ₃ /SiO ₂	2-Butene, 300 °C, 2 MPa, 4 h ⁻¹ , 2 g	X = 90%, S = 82%	[98]
8	WO ₃ /MgO/SiO ₂	2-Butene, 300 °C, 2 MPa, 4 h ⁻¹ , 2 g	X = 85%, S = 88%	[98]
9	WO ₃ /SiO ₂ -550 °C	2-Butene, 450 °C, 0.1 MPa, 1 g, 10 h	X = 68%, S = 40%	[99]
10	WO ₃ /SiO ₂ -650 °C	2-Butene, 450 °C, 0.1 MPa, 1 g, 10 h	X = 73%, S = 55%	[99]
11	WO ₃ /SiO ₂ -550 °C-imp	2-Butene, 450 °C, 0.1 MPa, 1 g, 10 h	X = 67%, S = 37%	[99]
12	WO ₃ /SiO ₂	2-Butene, 600 °C, 0.1 MPa, 3 g, 2 h	X = 60%, S = 49%	[100]
13	WO ₃ /SiO ₂ -cal-H ₂	2-Butene, 350 °C, 2 MPa, 3 g, 1 h	X = 71%, S = 91%	[101]
14	WO ₃ /SiO ₂ -H ₂	2-Butene, 350 °C, 2 MPa, 3 g, 1 h	X = 75%, S = 92%	[101]
15	W-SBA-15-N ₂	1-Butene, 450 °C, 0.1 MPa, 1.8 h ⁻¹ , 0.5 g	X = 88%, S = 69%	[102]
16	W-SBA-16	1-Butene, 450 °C, 0.1 MPa, 2 h ⁻¹ , 1 g, 3 h	X = 58%, S = 78%	[95]
17	W-KIT-6	1-Butene, 450 °C, 0.1 MPa, 2 h ⁻¹ , 1 g, 3 h	X = 59%, S = 79%	[95]
18	W-KIT-5	1-Butene, 450 °C, 0.1 MPa, 2 h ⁻¹ , 1 g, 3 h	X = 58%, S = 79%	[95]
19	WO ₃ /KIT-6	1-Butene, 450 °C, 0.1 MPa, 2 h ⁻¹ , 1 g, 3 h	X = 50%, S = 66%	[95]
20	WO ₃ /SiO ₂	1-Butene, 450 °C, 0.1 MPa, 2 h ⁻¹ , 1 g, 3 h	X = 47%, S = 61%	[95]
21	W-Al-KIT-6	1-Butene, 450 °C, 0.1 MPa, 0.8 h ⁻¹ , 1 g, 3 h	X = 78%, S = 82%	[103]
22	W-KIT-6	1-Butene, 450 °C, 0.1 MPa, 0.8 h ⁻¹ , 1 g, 3 h	X = 55%, S = 67%	[103]
23	WO ₃ /SiO ₂	1-Butene, 450 °C, 0.1 MPa, 0.8 h ⁻¹ , 1 g, 3 h	X = 37%, S = 89%	[103]
24	W-KIT-6 + MgO	1-Butene, 350 °C, 0.1 MPa, 0.4 h ⁻¹ , 1 g	X = 78%, S = 95%	[104]
25	W-FDU-12 + MgO	1-Butene, 450 °C, 0.1 MPa, 0.9 h ⁻¹ , 1 g	X = 79%, S = 90%	[105]
26	W/FDU-12 + MgO	1-Butene, 450 °C, 0.1 MPa, 0.9 h ⁻¹ , 1 g	X = 43%, S = 39%	[105]
27	WO ₃ /SiO ₂ + MgO	1-Butene, 450 °C, 0.1 MPa, 0.9 h ⁻¹ , 1 g	X = 34%, S = 10%	[105]
28	W-MCM-48 + MgO	1-Butene, 450 °C, 0.8 MPa, 3.2 h ⁻¹ , 0.38 g	X = 27%, S = 47%	[106]
29	WO _x /USY	<i>t</i> -2-Butene, 400 °C, 0.1 MPa, 0.27 h ⁻¹	X = 85%, S = 80%	[86]
30	WO ₃ /SiO ₂	<i>t</i> -2-Butene, 400 °C, 0.1 MPa, 0.27 h ⁻¹	X = 55%, S = 10%	[86]
31	WO _x /ZSM-5	<i>t</i> -2-Butene, 400 °C, 0.1 MPa, 0.27 h ⁻¹	X = 99%, S = 45%	[86]
32	WO _x /SAPO	<i>t</i> -2-Butene, 400 °C, 0.1 MPa, 0.27 h ⁻¹	X = 90%, S = 32%	[86]
33	WO _x /β	<i>t</i> -2-Butene, 400 °C, 0.1 MPa, 0.27 h ⁻¹	X = 91%, S = 35%	[86]
34	Re ₂ O ₇ /ANN	2-Pentene, 60 °C, 5.33 h ⁻¹ , 1 g	X = 87%, S = 38%	[107]
35	Re ₂ O ₇ /γ-Al ₂ O ₃	2-Pentene, 60 °C, 5.33 h ⁻¹ , 1 g	X = 65%, S = 18%	[107]
36	Re ₂ O ₇ /SO ₄ ²⁻ /ZrO ₂ -Al ₂ O ₃	1-Hexene, 60 °C, 0.1 MPa, 2 h ⁻¹ , 10 min	X = 99%, S = 75%	[15]
37	Re ₂ O ₇ /B ₂ O ₃ -Al ₂ O ₃	1-Hexene, 60 °C, 0.1 MPa, 2 h ⁻¹ , 10 min	X = 92%, S = 73%	[15]
38	Re ₂ O ₇ /SO ₄ ²⁻ /ZrO ₂ -Al ₂ O ₃	1-Heptene, 60 °C, 0.1 MPa, 2 h ⁻¹ , 10 min	X = 99%, S = 78%	[15]
39	Re ₂ O ₇ /B ₂ O ₃ -Al ₂ O ₃	1-Heptene, 60 °C, 0.1 MPa, 2 h ⁻¹ , 10 min	X = 98%, S = 50%	[15]
40	Ru 5e	Cyclooctene, 60 °C, 2.1 MPa, 5 h, 0.5% _{cc}	X = 60%, S = 56%	[51]
41	Ru-20 complex	Cyclooctene, 35 °C, 1 MPa, toluene	X = 96%, S = 53%	[108]
42	Ru-20 complex	Norbornenes, 35 °C, 1 MPa	X = 94%, S = 95%	[108]
43	Mo-SiAlO _x	2-Butene, 50 °C, 0.13 MPa, 22 ml·min ⁻¹ , 0.02 g	<i>r</i> = 203 mmol·g ⁻¹ ·h ⁻¹	[109]
44	W-SiAlO _x	2-Butene, 50 °C, 0.13 MPa, 22 ml·min ⁻¹ , 0.15 g	<i>r</i> = 2.2 mmol·g ⁻¹ ·h ⁻¹	[109]
45	MoO ₃ -Al ₂ O ₃ -SiO ₂	2-Butene, 50 °C, 0.13 MPa, 22 ml·min ⁻¹ , 0.02 g	<i>r</i> = 45 mmol·g ⁻¹ ·h ⁻¹	[109]
46	Mo/SBA-15	2-Butene, 50 °C, 0.13 MPa, 22 ml·min ⁻¹ , 0.02 g	<i>r</i> = 20 mmol·g ⁻¹ ·h ⁻¹	[109]
47	Mo complex	Cyclooctene, 80 °C, 3 MPa, 6 h, toluene	X = 30%, TON 30,000	[110]

Note: Conversion = 1 – (final moles of reactants)/(initial moles of reactants) × 100%; Selectivity = (moles of ethenolysis products)/(moles of ethenolysis products + cross-metathesis products + self-metathesis products) × 100% (note: the stoichiometric numbers should be consider for different substrates); TON = mols of ethenolysis product/mols of catalyst.

H₂O pretreatment can cause a complete loss of metathesis activity of W-SBA-15 due to the aggregation of isolated WO_x species and the formation of inactive crystalline WO₃ phase [102]. Zhou *et al.* [95] incorporated W species on ordered mesoporous silicates, W-SBA-16 and W-KIT-6, which outperformed impregnated WO₃/KIT-6 and the supported WO₃/SiO₂ catalysts for the metathesis of 2-butene with ethylene at 450 °C (Table 2, #16–20). During one-pot synthesis, delaying the time to add the W precursor can have more active W species on the surface and thus improve the catalytic performance. The recyclability study revealed very little loss of activity in five-days reaction. The reaction mechanism study indicated a similar route to the W-SBA-15 as shown in Fig. 10.

W-KIT catalysts. Zhou *et al.* [103] using one-pot method to synthesize ordered W and Al co-doped mesoporous W-Al-KIT-6 catalyst which displayed higher performance than the W-KIT-6 for 1-butene to propene (X = 78%, S = 82%, Table 2, #21–23). The introduction of Al species can generate more acidic sites, larger surface

area, and higher W dispersion without changing the 3D ordered mesoporous structure of KIT-6 as confirmed by the TEM images (Fig. 11(a), (b)). The acid sites can accelerate the isomerization and metathesis reaction of 1-butene to 2-butene and propene, respectively. However, excess Al may cause pore structure collapse and poor activity. W-KIT-6 catalyst was synthesized by one-pot direct hydrothermal method and applied for converting 1-butene to propene in the presence of MgO by Zhou's group (Table 2, #24) [104]. The increased W loading can improve the catalytic activity to some content. However, further increased W loading led to the formation of aggregated WO₃ species and the collapse of the mesoporous structure as shown in the TEM images (Fig. 11 (c), (d)).

W-FDU-12 catalyst. Zhou *et al.* [105] prepared W based mesoporous FDU-12 catalyst by an one-pot hydrothermal process (doped W-FDU-12) which displayed a higher activity for the 1-butene ethenolysis in the presence of MgO compared to the sup-

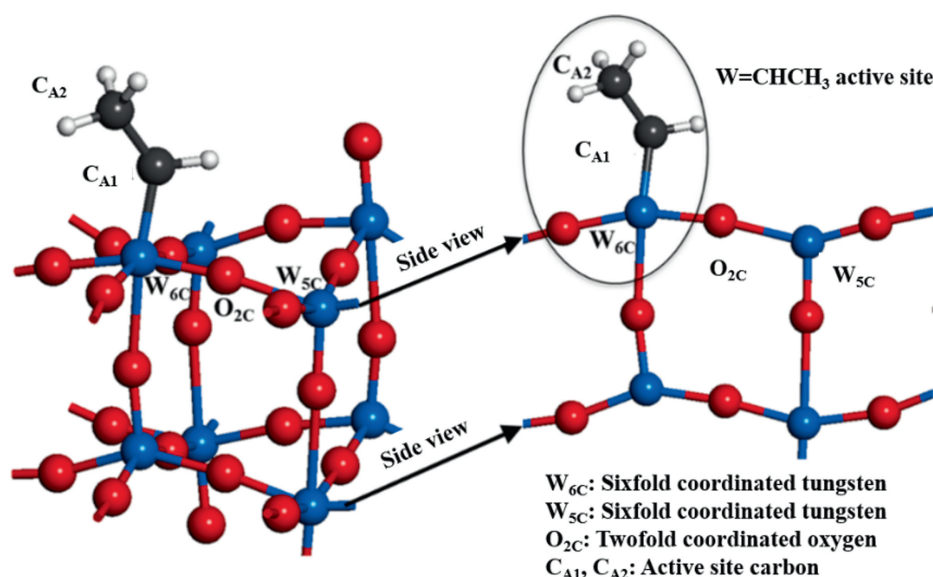


Fig. 9. Geometry-optimized WO_3 (001) surface with $\text{W} = \text{CHCH}_3$ active site [94].

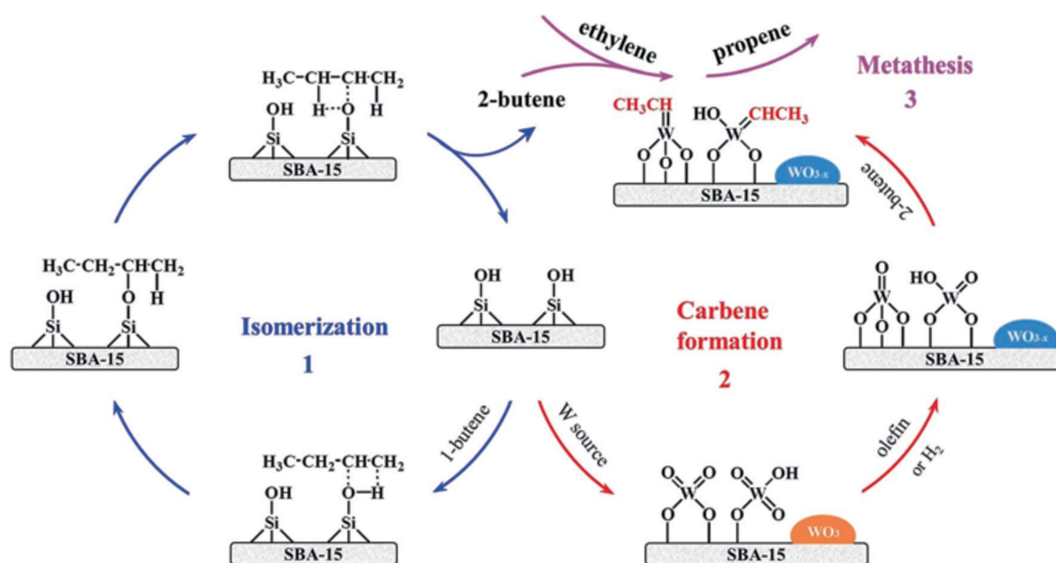


Fig. 10. Proposed route for metathesis of 1-butene over W-SBA-15 catalysts: (1) isomerization, (2) carbene formation, (3) metathesis reaction [102].

ported WO_3/SiO_2 and $\text{WO}_3/\text{FDU-12}$ catalysts (Table 2, #25–27). The good activity of the doped W-FDU-12 catalyst is ascribing to the presence of highly dispersed W^{5+} ($\text{W}=\text{O}-\text{Si}$) active species whereas the supported catalysts contained only the bulk aggregated WO_3 (W^{6+}) species as confirmed by XPS results and the TEM images (Fig. 12(a), (b), (c)). W-FDU-12 catalyst showed lower activity and faster deactivation at lower temperature due to the formation and deposition of heavy organic compound.

W-MCM-48 catalyst. W incorporated MCM-41 and MCM-48 catalysts were synthesized and evaluated in the producing propene from 1-butene and ethylene (Table 2, #28) [106]. The catalytic activity decreased as follows: $\text{WO}_3\text{-MCM-48} > \text{WO}_3\text{-MCM-41} > \text{WO}_3/\text{SiO}_2$. The best activity of W-MCM-48 catalyst was ascribing to the highest dispersity of WO_3 and greatest acidic acid sites as evidenced from TPD- NH_3 . The diffuse reflection UV–visible spectrophotometer (DRS–UV–Vis) results revealed that both W-MCM-41 and W-MCM-48 have more tetrahedral WO_3 species than octahedral W species. The isomerization and the metathesis reac-

tion of 2-butene can be promoted by higher operation temperature as proved by the thermodynamic analysis method [106]. The reaction pressure was found had little effect to the catalytic performance of both catalysts.

WO_x/USY catalyst. Tsang *et al.* [86] entrapped single W site through Brønsted acid sites on the inner surface of the zeolite cavity, such as USY, ZSM-5, SAPO and β zeolite, by wet impregnation method. WO_x/USY exhibits the best activity (Table 2, #29–33) and good stability in 20 h reactions ascribing to the well isolation of WO_x in pores as evidenced by the high-resolution scanning transmission electron microscopy (STEM, Fig. 12(d), (e)). The replacement of WO_x in atomic proximity to BAS also contributed to the high metathesis efficiency. Unoccupied Brønsted acid sites facilitated olefin adsorption and metalocycle intermediates formation over WO_4 MASs. That explained the 7300 times higher propene formation rate over WO_x/USY ($X = 99\%$, $S = 80\%$) than the industrial WO_3/SiO_2 catalyst. WO_x/USY was stable when it was tested in a wide range of conditions.

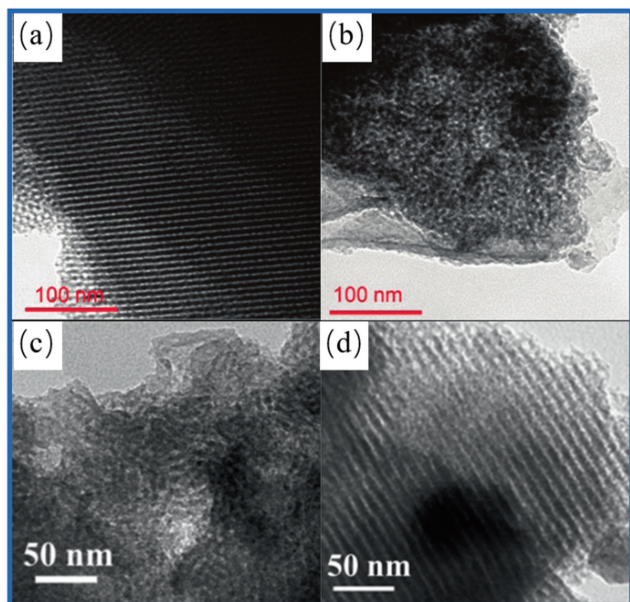


Fig. 11. TEM images of (a) W-Al-KIT-6-10 [103], (b) W-Al-KIT-6-1 [103], (c) W-KIT-6-15 [104], and (d) W-KIT-6-25 [104].

4.2. Re-based catalysts

Re-based catalysts are highly active and selective for metathesis of light olefins at low temperature [115]. The nature of the supports has significant effect to the activity and stability of the Re-based catalyst [116]. The volatility of rhenium heptoxide may lead to Re loss during the calcination and regeneration steps [117].

Mutin *et al.* reported Re-based catalyst with outstanding performance in the metathesis reaction of *trans*-2-butene to propene [19]. They noticed that the sublimation of Re heptoxide is main reason of the Re loss during the calcination step. Non-hydrolytic sol-gel method using anhydrous conditions can form Re-Si-Al mixed oxide catalyst and avoid Re loss. $\text{Re}_2\text{O}_7\text{-SiO}_2/\text{Al}_2\text{O}_3$ catalysts were amorphous with mesoporous textures and acidity. Panpranot *et al.* [107] supported Re_2O_7 on aluminum nitrate (ANN) to obtain $\text{Re}_2\text{O}_7/\text{ANN}$ catalyst which has small pore size and pore volume. However, this catalyst showed enhanced conversion of 2-pentene and selectivity to propene than the commercial $\gamma\text{-Al}_2\text{O}_3$ supported Re_2O_7 catalyst (Table 2, #34,35) ascribing to the larger population of acidic OH groups and Lewis acid sites which promoted the formation of the Re oxide active species [107]. $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ has higher Brønsted acidity, which accelerated the oligomerization and/or polymerization reactions to form C^{5+} products and promoted the coke formation. They further explained the mechanism of active sites formation. If ReO_4^- replaced the most basic OH groups, it will form inactive sites. If ReO_4^- replaced more acidic OH groups, it will form active sites. In the case of $\text{Re}_2\text{O}_7/\text{ANN}$, ReO_4^- mainly replaced the acidic OH groups and generated more Lewis acidity and less Brønsted acidity as conformed by the *in-situ* IR spectra. Glazov *et al.* [15] synthesized $\text{Re}_2\text{O}_7/\text{SO}_4^{2-}/\text{ZrO}_2\text{-Al}_2\text{O}_3$ and $\text{Re}_2\text{O}_7/\text{B}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts and tested metathesis reaction of 1-hexene and 1-heptene with ethylene to produce propene (Table 2, #36–39). The results showed that propene formed as the main product within 10 mins. After 10 min reaction, more and more C_9+ products formed due to the oligomerization of the products and the deactivation of active centers for metathesis reaction. Furman *et al.* [118] carried out metathesis reaction of cyclohexene in the presence of ethylene and $\text{NH}_4\text{ReO}_4/\text{Al}_2\text{O}_3$ catalyst and obtained 25% conversion and 99.9% selectivity to octadiene-1,7.

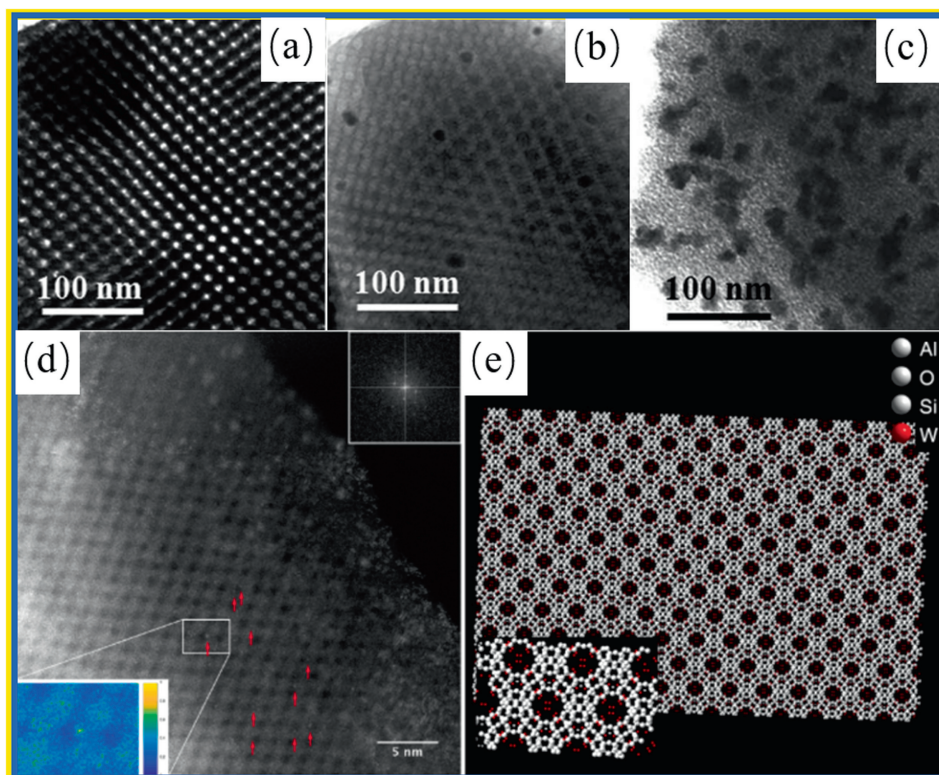


Fig. 12. TEM images of (a) doped W-FDU-12 [105], (b) supported W/FDU-12 [105], and (c) WO_3/SiO_2 [105]. (d) HAADF-STEM image of WO_x/USY [86], (e) the crystallographic model of WO_x/USY [86].

The catalyst shows good stability in six cycles with intermediate regenerative treatments.

4.3. Ru-based catalysts

Ru-based catalysts were the most reported active catalysts for metathesis reactions, e.g. G1, G2, HG1 and HG2. Tang *et al.* [33] immobilized Ru on NHC and evaluated for the metathesis of 5-decene with ethylene to 1-hexene. Ru-NHC (Fig. 13(a), Ru431) showed much higher performance than the Grubbs and HG catalysts. In this process, the catalytic activity decreased in the order of Ru431 > HG2 > G2 > HG1 > G1 ascribing to the higher activity of NHC based catalysts compared to the phosphine-based analogues. This was also confirmed by the higher activity of HG2 and HG1 compared to the G2 and G1 catalysts respectively. Most Ru-based catalysts existed in the Ru methylidene form undergo rapid decomposition, due to the attack of nucleophilic phosphine ligands. However, Ru431 has more bulky substituents around the metal center and improved stability. Hong *et al.* [49] synthesized F-ImPy-Ru (Fig. 1, Ru217) catalysts and investigated the metathesis of cyclooctene (Table 2, #40). Ru217 bearing a structurally unsymmetrical ImPy ligand ($S = 22\%$) showed higher selectivity compared to the Grubbs Ru catalyst bearing symmetrical NHCs ($S = 12\%$). They found the selectivity to the target product decreased at higher ethylene pressure due to the decomposition of the Ru catalyst.

In order to compare the effect of ligand, Togni *et al.* [108] synthesized four groups of homologous Ru-based metathesis catalysts and evaluated for *cis*-cyclooctene metathesis with ethylene to produce α,ω -diene (Fig. 13(b)). Group 1 has symmetrical saturated NHCs. Group 2 has unsymmetrical saturated NHCs. Group 3 has unsaturated NHCs. Group 4 has *N*-trifluoromethyl (*N*-CF₃) benzimidazole NHCs. Comparing to the G2 catalyst, Group 4 catalyst displayed significantly superior performance (Table 2, #41,42), due to the higher π -acceptor properties of *N*-CF₃ NHCs which increased the rotation barrier around the Ru–C_{NHC} bond and the configurational stability of diastereomeric methylidene species [108]. Dissymmetry at the NHC ligand was recognized as a key factor for tuning the products distribution [108]. Plenio *et al.* [119] studied the initiation mechanism of ethylene with HG catalyst via UV–Vis spectroscopy. They found ethylene initiates the HG complexes, especially the electron-rich complexes, apparently more slowly than longer chain 1-hexene. They collected the species has been

discussed in either experimental or DFT calculation work as the possible intermediates of the initiation of HG complex. Complex II has been ruled out due to the small activation barrier to form the ruthenacyclobutane (RCB), Piers's group reported that the release of the complex IV with a η^2 -vinyl bound styrene has a significant activation barrier [120]. The RCB (complex III or complex VI) has been reported as accepted intermediate of the multistep reaction (Fig. 13(c)) [119]. Complex III containing 2-isopropoxyphenyl group is less likely the intermediate, because the strong metal-to-ligand charge transfer absorbance of the complex III has not been observed [120,121]. The unsubstituted RCB (complex VI, Fig. 13(c)) is more stable than the monosubstituted RCB [122,123]. Furthermore, the observed absorbance is well-matched with complex VI as an intermediate. Hence, the ruthenacyclobutane complex VI is most likely the intermediated in the ethenolysis reaction with HG complexes.

4.4. Mo-based catalysts

Mo-SiAlO_x, W-SiAlO_x, MoO₃-Al₂O₃-SiO₂ and Mo/SBA-15 catalysts were synthesized by impregnation method and tested for metathesis of butene with ethylene to produce propene [109]. The propene formation rate over Mo-based catalysts is almost 100 times higher than that of W-based catalysts (Table 2, #43–46) due to the generation of more carbenes on the surface of the Mo catalysts. They developed a titration method to quantify the amount of active carbenes species in the metathesis of 2-butene over Mo- or W-based catalysts. It is well accepted that $M = CHCH_3$ type carbenes can form propene, rather than $M = CH_2$ type. Hence, the propene formation rate increases with the growing number of carbene species formed from the supported MoO_x or WO_x species. Kondratenko *et al.* [20] probed the effect of the prebeds on the rate of propene formation and the catalyst stability by locating CaO, Al₂O₃, or SiO₂-Al₂O₃ as upstream of MoO_x/SiO₂-Al₂O₃ catalyst. These materials, especially CaO, enhanced the metathesis activity of the MoO_x based catalyst by purifying the feed components to get rid of the poisoning impurities. Furthermore, the prebeds can generate gas-phase promoters to stabilize and form active Mo carbene species. Buchmeiser *et al.* [110] synthesized novel Mo imido alkylidene NHC complexes by the reaction with diacetone silver tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate ([Ag(CH₃CN)₂] BAr_F, Fig. 14). This complex showed a TON up to 30,000 for metathesis of cyclooctene with non-purified ethylene at a pressure

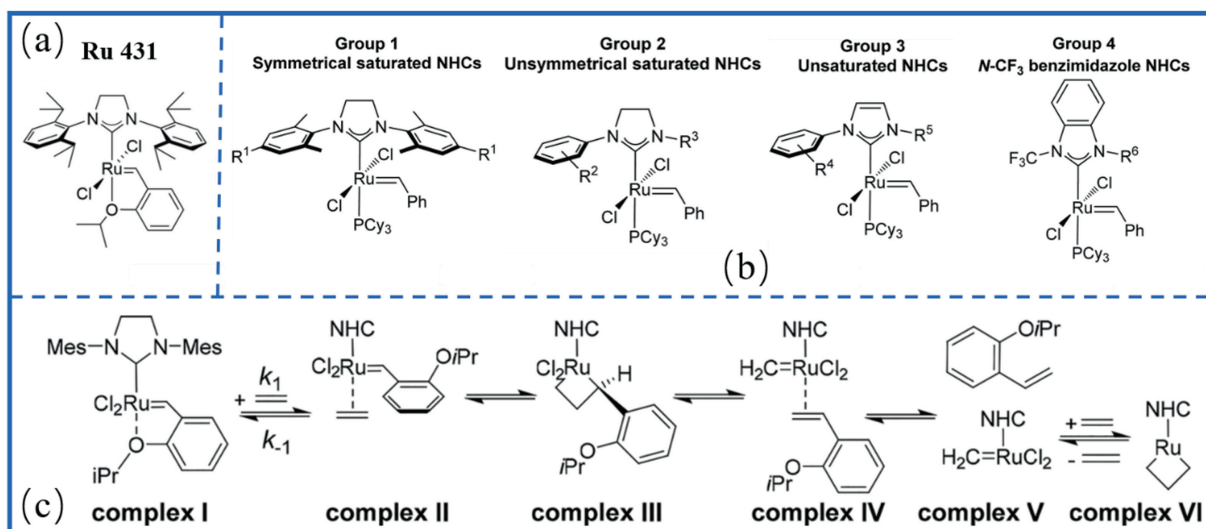


Fig. 13. (a) The illustration of Ru 431 [33], (b) Four groups of Ru-based catalysts for cyclooctene ethenolysis [108], (c) Key steps in the ethylene-induced initiation of HG complexes [119].

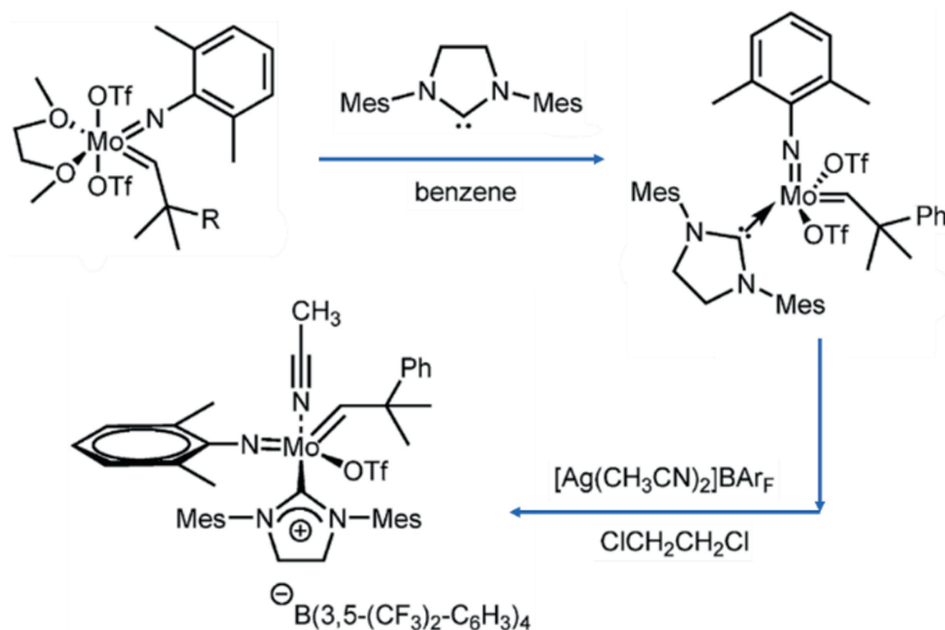


Fig. 14. Synthesis of novel Mo imido alkylidene NHC complex [110].

of 3 MPa and 80 °C (Table 2, #47). The NHC ligand can stabilize the cationic charge at Mo. However, this catalyst did not display any reactivity for functional olefins. Some multifunctional catalysts and strategies have been proposed for producing propylene in ETP processes through successive dimerization/isomerization/metathesis reactions using only ethylene as a raw-material, such as Mo-Ni [124], Ni-MCM catalysts [6], Ni-AIKIT-6 [5] and HZSM catalyst [125].

5. Conclusions and Outlooks

There are several factors affected the catalytic performance of W- and other metal-based catalysts for the ethenolysis reaction of butene to produce propene. (1) Metal loading. As the metal increased, the catalytic activity of the catalysts increased to some extent. Access of metal content sometime will cause the collapse of the mesoporous structure of the catalysts. On the other hand, access of metal loading may form bulk metal oxides species which were reported inactive for olefin metathesis reaction. Both situations will lead to a decrease of the activity and selectivity. (2) The reaction temperature played a significant role of the catalytic activity and selectivity towards propene. As the reaction temperature increased, the catalytic activity increased. At low temperature, the production of heavy compounds will cause catalysts deactivation. (3) Gas pretreatment has significant effect to the catalytic activity. Studies showed that O₂, N₂, H₂, or the mixture of N₂ and H₂ could improve the catalytic activity of the catalyst. However, water treatment may cause the catalyst deactivation due to the transformation of active metal sites to inactive metal oxides. The calcination can regenerate the deactivated catalyst by removing the water and regenerated the active metal species with slight activity decrease. (4) The calcination temperature also affected the catalytic activity. Usually, the catalytic activity increase as the calcination temperature increased. However, to some extent, the high calcination temperature may cause the collapse of the catalyst structure and formation of inactive metal oxides. (5) Brønsted and Lewis acidity have effect to the catalytic performance for the ethenolysis reactions. Unoccupied Brønsted acid may facilitate olefin adsorption and metallocycle intermediates formation. (6) The synthesis methods and the types of the support determined the

dispersity of the metal species. Higher surface area is good for getting a high dispersed metal species which is more active and selective in ethenolysis reactions.

The achievement in the area of oleochemical ethenolysis have been systematically summarized and discussed in this mini review. The effects of various factors have been concluded in this work. The key findings in this work include:

- (1) The structure of the complexes plays significant role in determining the electronic properties of Ru active centers. Ethenolysis of complex with CAAC ligands mainly displayed lower reaction rate but higher durability than that with NHC and Ph ligands.
- (2) The operating conditions, such as ethylene pressure, reaction temperature, also have effect to the catalytic activity. As the ethylene pressure increases, the solubility increases, thus the catalytic activity can be improved. However, there is a balance between the good activity and catalyst poison (inhibition) at high pressure of ethylene.
- (3) Immobilized Ru complexes have apparent advantages over the homogeneous complex for catalyst preparation, separation, and regeneration. Although the supported Ru complex displayed lower activity compared to the homogeneous Ru complex, the immobilized Ru complex still has great potential to replace the homogeneous Ru catalyst.

There are two major issues plaguing current ethenolysis catalysts: (1) low activity and selectivity caused by the existence of complicated functional groups in triglycerides; (2) short lifetime and high cost of synthesis, separation, and regeneration of the catalysts. The further study should focus on the cost-effective methodology on catalyst synthesis for highly active heterogeneous catalysts based on fundamental understanding of the reaction mechanism for oleochemical ethenolysis.

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.

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