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# Catalytic hydrogenation of C=C and C=O in unsaturated fatty acid methyl esters

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## Abstract

Biodiesel derived from edible and non-edible oils has received much attention as a chemical feedstock or as a raw fuel alternative to the traditional diesel due to its renewability and biodegradability. However, the crude biodiesel containing large amounts of polyunsaturated fatty acid methyl esters (FAMEs) is susceptible to oxidation upon exposure to heat, light, and oxygen. Catalytic hydrogenation of biodiesel has been considered as a feasible and powerful technique to improve the oxidative stability of biodiesel and hence to provide stable raw materials for industrial applications. The catalytic hydrogenation of FAMEs is a complex process but basically consists of hydrogenation of C=C or C=O, depending on the desirable properties of final products. In this review, we summarize recent developments in hydrogenation of C=C and C=O in FAMEs with focus on catalysts, reaction mechanisms, and reactor conditions. The features of hydrogenation of FAMEs are generalized and the opportunities for future research in the field are outlined.

*Keywords*: Biodiesel; Unsaturated methyl ester; FAME; Hydrogenation; Catalysis; Reactor design.

# Contents

# 1. Introduction

The increased demand for sustainable energy has attracted much interest for the development of alternative fuels to that derived from traditional petroleum oil. Biodiesel derived from vegetable oils and animal fats has been considered to be an important alternative to the diesel fuel.[1-4] Taking into account the raw source of biodiesel, it can be defined as a renewable fuel with high biodegradability. Currently biodiesel is mainly produced by esterification of fatty acids or by transesterification of oils with methanol in the presence of an alkali catalyst, and there have been many reviews regarding this topic.[5-13] The resulting biodiesel from transesterification has the same fatty acid profile as the parent oil or fat which contains a large amount of double bonds in the carbon chains. In this case, the biodiesel is not stable and can transform into peroxide, aldehyde, and ketone etc. in the presence of light, heat, and oxygen.[14,15] Thus, the oxidative stability of biodiesel containing unsaturated FAMEs is of great concern in this field.

A direct way to improve the oxidative stability of biodiesel is the addition of antioxidants to the fuel. However, the high costs of antioxidants and the relatively low effectiveness of this method[16,17] limit its wide application. Another alternative to the above method is chemical modification of biodiesel, such as hydrogenation, hydrodeoxygenation, and decarbonylation etc. Compared to decarboxylation and decarbonylation that involve the loss of one carbon atom in the form of CO or $CO_2$, hydrogenation and hydrodeoxygenation maintain the same carbon chain length as the original fatty acid molecule. All these hydro-treating techniques have been received much attention in the past decades and are under intensive studies. Our interest here concerns the hydrogenation which can be operated under moderate conditions and is favorable for an industrial-scale production. Hence, this review is limited to the scope of hydrogenation rather than the complete array of hydro-treating techniques. The possible reactions that may occur during hydrogenation of unsaturated FAMEs are shown in Fig. 1. Note this figure does not show *cis-trans* isomerization reactions, which always accompany hydrogenation reactions.[18] Basically, polyunsaturated FAME can be hydrogenated into monounsaturated or saturated methyl esters through C=C hydrogenation or into fatty alcohols by the C=O hydrogenation. At the same time, the produced fatty alcohols can react with the methyl ester to form new longer chain esters through transesterification. Complete hydrogenation of unsaturated FAMEs or fatty alcohols would lead to the removal of oxygen and the formation of saturated hydrocarbons.

The desirable chemical reactions during hydrogenation of FAMEs in biodiesel depend on the application of the product. There are two basic uses for the hydrogenation products: one is as fuel in combustion engines and the other is as chemical intermediates to obtain other valuable chemicals.[19] For the former purpose, the products obtained should have comparably high oxidative stability and preserve good cold flow properties that are required for fuel used in a combustion engine. Among all the possible products from hydrogenated biodiesel, monounsaturated *cis*-FAMEs with moderate melting points and stability are preferable to saturated or *trans*-FAMEs which are structurally more stable but have relatively higher melting points. Thus, it is desirable to avoid or minimize complete hydrogenation of FAMEs and *cis-trans* isomerization during the hydrogenation of biodiesel if the product is assumed to be used as a fuel in an ignition engine. This process is well known as partial hydrogenation, which purposely hydrogenates polyunsaturated FAMEs into *cis*-monounsaturated ones. As for the latter purpose, the most common products from FAME hydrogenation are fatty alcohols which are raw materials in the production of detergents and surfactants and are also important components of cosmetics and foods. The chemical reactions in this process mainly involve hydrogenation of C=O in FAMEs.

Hydrogenation reactions can be operated both in absence and presence of a catalyst, depending on the desirable properties of the final products. Compared to non-catalytic hydrogenation process, the use of a suitable catalyst is supposed to increase the reaction rate and enable the reaction at lower temperatures. It may be argued that hydrogenation at relatively low temperatures can also be achieved by introduction of metal-hydride reagents, such as $LiAlH_4$, to FAME without catalyst. However, this process requires recovery and regeneration of the hydrogen carrier and may generate large amounts of waste compared to hydrogenation using $H_2$ as the reducing agent. More importantly, in non-catalytic hydrogenation, it is generally difficult to control the selectivity of the chemical reactions. On the contrary, the presence of a catalyst in hydrogenation reactions can provide a better possibility to control selectivity towards the desired products. Thus, catalytic hydrogenation of FAME has been recognized as one of the most promising techniques for chemical modification of biodiesel. Falk and Meyer-Pittroff showed that almost 100% saturation of FAMEs produced from fats of rendering plants and used cooking oils (Fig. 2) could be achieved using a commercial Ni catalyst (B113W, Degussa, Germany).[20] The oxidative stability of the FAMEs was increased several times due to its increasing saturation via hydrogenation, depending on the feed source, as shown in Fig. 2.

Actually catalytic hydrogenation has a long history and is widely used in the current petrochemical industry. Veldsink et al. presented a comprehensive literature review of heterogeneous hydrogenation of vegetable oils in 1997 with a focus on kinetics of mainly Ni-based catalysts.[21] Since advances have been made in this field especially concerning catalyst screening and selectivity, this review attempts to give an overview of recent developments in catalytic hydrogenation of FAMEs with emphases on catalyst fomulations, reaction mechanism, and reactor configuration.

## 2. Catalyst and reaction mechanism

As mentioned above, hydrogenation of FAMEs may involve different chemical reactions according to the intended purposes, namely, C=C partial hydrogenation and C=O hydrogenation. Since the nature of the two functional groups is different, the conditions for hydrogenation of them diverge significantly. The average bond enthalpy, representing the energy to break a C=C bond (614 kJ/mol) is lower than that of breaking a C=O bond (799 kJ/mol) though the exact bond enthalpy of a particular chemical bond depends upon the molecular environment. Thus, hydrogenation of a C=C double bond in FAMEs is thermodynamically favored over C=O hydrogenation. In addition, the weaker polarization of the C=O bond and steric hindrance may also be responsible for its lower reactivity compared to the C=C double bond,[22] which consists of a sigma ($\sigma$) bond and a highly reactive pi ($\pi$) bond. However, the preference for C=C or C=O hydrogenation depends on the applied catalyst. The selectivity (C=O vs. C=C group hydrogenation) can be controlled by the metal used as catalyst, the presence of a second metal, metal particle size, dispersion, electron-donating or -withdrawing ligand effects induced by the catalyst support material, steric constraints in the metal environment and strong metal-support interactions.[23] Hence the catalysts for FAME hydrogenation can be basically categorized into two different types according to their selectivities.

## 2.1. C=C partial hydrogenation

### 2.1.1. Catalyst

Partial catalytic hydrogenation of C=C double bond with hydrogen has been investigated on parts of VIII group metals, such as Ni, Co, Pd, Pt, and Rh. These metals are also widely used for other catalytic reactions, such as hydrocarbon reforming,[24-29] and $CO/CO_2$ hydrogenation.[30-35] These metal-containing catalysts can basically be divided into two families: heterogeneous and homogeneous, depending on the phases between the catalyst and the reactants. Both homogeneous and heterogeneous catalysts have been studied for partial hydrogenation of FAMEs. Fell and Schäfer investigated the partial hydrogenation of methyl linoleate on Ziegler-type catalysts containing Ni, Co, or Pd metals and selectivities higher than 90% to C18:1 esters were measured.[36-38] In particular, Rh-based complexes exhibited high catalytic activity towards partial hydrogenation of polyunsaturated crude methyl esters of linseed and sunflower oils into monounsaturated counterparts.[39-43] Under optimized operating conditions, a selectivity of 79.8% towards C18:1 FAME could be achieved for the linseed, sunflower, and soybean oils.[42] Simultaneously, however, relatively high concentrations of *trans*-C18:1 in the range of 10-42 mol% was observed. Recently, Spasyuk et al. found that an Osmium dimer based catalyst to be particularly efficient for C=C hydrogenation of methyl hexanoate. An almost 100% conversion of the methyl hexanoate was achieved in 2 hours at 100 $^{o}C$ and hydrogen pressure of 5 MPa by using only 0.05 mol.% of the catalyst.[44] The performance of the catalyst towards hydrogenation of a FAME with more than one C=C bond was, however, not studied. Thus, it is still unclear whether this homogeneous catalyst containing Os can be extended to control partial hydrogenation reactions.

Though the reported homogeneous catalysts appear to be active and selective for C=C hydrogenation, they always suffer from the problems of separation and regeneration. It may be argued that homogeneous catalyst may be only partly soluble in the reactants and hence can be separated. However, the separation time in this case, depending on the interfacial tension and the mutual solubility of the two phases, is still longer than that for heterogeneous catalysts. In terms of separation and regeneration, as well as operation modes in a reactor, heterogeneous catalysts are more preferable. For instance, Papadopoulos et al. claimed that the heterogeneous catalyst rhodium sulfonated phosphite (Rh/STPP) has an advantage over their previous homogeneous Rh/TPPTS catalyst in terms of the separation aspect.[14]

The majority of practical heterogeneous catalysts for FAME hydrogenation are solids, which basically consist of a metal and a support. Among the metals under investigation, Ni-based catalysts appear to be a good choice and, in particularly, RANEY nickel has been measured to have high activities in various hydrogenation reactions.[45-49] Actually, commercial hydrogenation of vegetable oils in the food industry is performed on Ni-based catalysts thanks to low price and rich abundance of nickel compared to noble metals.[50,51] Recent partial hydrogenation of polyunsaturated FAMEs on commercial Ni-based catalysts was also reported to considerably improve the quality of biodiesel.[20,52-54] For Ni-based catalysts, several studies have been directed towards the reaction kinetics of partial hydrogenation. A detailed summary on the kinetics for hydrogenation of vegetable oils over Ni-based catalysts has been reported by Veldsink et al.[21] The kinetic studies have not only provided an important guide how to design hydrogenation reactors, but also shed light on understanding the behavior of Ni towards hydrogenation reactions. The main issue under debate is the reaction mechanism of FAME hydrogenation over Ni-based catalysts. It is well known that the Langmuir-Hinshelwood-Hougen-Watson (LHHW) with reasonable assumptions is a fundamental approach for derivation of kinetic rate expressions of catalytic reactions. For FAME hydrogenation reactions, non-competitive adsorption of $H_2$ and FAME on different active sites was proposed in the LHHW model and could be used to fit the experimental data well, such as for hydrogenation of methyl oleates[55] or soybean oils[56] on Ni-based catalysts. However, the possibility of competitive adsorption was not taken into account in these kinetic studies. Recently, Cabrera and Grau reported the kinetics of the hydrogenation and *cis-trans* isomerization of methyl oleate on a Ni/$\alpha$-$Al_2O_3$ catalyst in the absence of mass-transport limitations.[57,58] The experimental kinetic data were fitted by several models, e.g. the classical LHHW based on non-competitive, competitive, and semi-competitive adsorption. It was found that the models derived from competitive adsorption between $H_2$ and organic species provided a better fit to the experimental data than the non-competitive adsorption. However, the statistical certainty from the mathematical viewpoint was not sufficient to discriminate the models based on the competitive and the semi-competitive adsorption, respectively. Further work is still needed to find more accurate kinetic representations of the reaction mechanism for partial hydrogenation of FAME on Ni-based catalysts.

Besides Ni, supported copper is another attractive non-noble metal catalyst for partial hydrogenation reactions. In the field of edible oil hydrogenation, Cu-based systems have traditionally been used due to a high selectivity for the reduction of linolenate C18:3 to C18:1 without affecting oleate.[59-63] Ravasio et al. showed that $Cu/SiO_2$ catalysts were effective and selective in the partial hydrogenation of rapeseed oil methyl esters.[64] A content of C18:1 as high as 88%, of which 20% was *trans*- product, was obtained after the partial hydrogenation, and the amount of C18:0 was not modified during the process. Ravasio et al. also investigated the performance of the catalyst for the hydrogenation of non-food oil methyl-esters.[61] The oils, which were rich in C18:3 or C18:2, could be easily hydrogenated to monounsaturated methyl ester with limited formation of C18:0. The molar content of *trans*-monounsaturated FAME in the final product was in the range of 12-20%.[62] Furthermore, the products obtained by hydrogenation of the oils from different plants using the supported copper catalyst were claimed to meet the European regulations in terms of cetane number and iodine value. For instance, the oxidation stability was improved from 1.2 to 5.3 h for the linseed oil, and from less than 1 to 4 h for the tall oil methylesters. Compared to the other common metals, the main advantage of Cu is that it does not show activity toward monoene reactions. Hence, the percentage of saturated FAMEs almost remains unchanged during the hydrogenation process, being favorable for keeping relatively low melting points of the product. Besides the selectivity toward C=C hydrogenation, there are some new applications of Cu in biodiesel production processes. Recent studies have showed that the combination of Cu and alkaline earth metal oxides could serve as bi-functional catalysts for transesterification or esterification to produce biodiesel and partial C=C hydrogenation.[65-67] This considerably simplifies the process from the raw materials to the final product which can be used directly. Thus, as Cu is a relatively inexpensive metal, it remains to be an attractive catalyst in the field of biodiesel hydrogenation.

The heterogeneous catalysts containing noble metals, e.g. Rh, Pd, Ru, and Pt, have also been extensively investigated, especially towards hydrogenation of natural oils which have the same fatty acid profiles as biodiesel. It was reported that the activity order for the hydrogenation of natural oils on different noble metals followed the order Pd > Rh > Pt > Ir > Ru > Ni.[68,69] In an additional study, Pd was also reported to be more active than Pt and Ni towards partial hydrogenation of rapseed oil-derived FAMEs.[70] Dijkstra proposed that the difference observed for these noble metals might be related to the physical properties (surface area and metal dispersion) of the catalysts and the chemical nature (adsorption bond strength) of the metals.[69] For metal catalysts in heterogeneous catalysis, the *d*-band center is sometimes used as a descriptor of the chemisorption strength.[71] In fact, if the relative activity for the C=C hydrogenation is plotted with respect to the *d*-band center, there appear (with the exception of Ir) to be a volcano-like relation (Fig. 3). The volcano relation may originate from the Sabatier principle which describes reactivity and interaction between reactant and catalyst surface. Specifically, if the interaction is too weak, the reactant may have difficulties to bind to the surface of the catalyst and hence the reaction will be slow; if the interaction is too strong, the species, e.g. reactants, intermediates, products, involved in the catalytic reaction may block the catalyst surface, leading to a low reaction rate. The reason why Ir does not follow the general trend may be due to limitations of the *d*-band center model. It is also possible that there are other factors such as surface area and metal dispersion that affect the observed activity of Ir towards C=C hydrogenation. Thus, further studies are needed to clarify the nature of the differences among these metals towards hydrogenation.

According to the activity order presented in Fig. 3, Pd seems to be the most promising metal for partial hydrogenation of C=C in FAMEs. However, it should be kept in mind that the aim of partial hydrogenation of FAMEs is not limited to the reduction of polyunsaturates into monounsaturates, but also the formation of *trans* products should be avoided because of the high melting points of these products. The activity order of the noble metals toward the *cis*-*trans* isomerization was found to be Pd > Rh > Ru > Pt.[69] In this respect, Pd appears not to be the most suitable catalyst for partial hydrogenation of FAMEs. In order to make Pd more attractive in this field, several studies have been conducted to decrease its activity towards *cis*-*trans* isomerization. It was found that *cis*-*trans* isomerization during partial hydrogenation of FAMEs on a Pd catalyst could be relieved by controlling the reaction conditions. For instance, under supercritical or near-critical conditions of propane, a relatively low *trans*-fatty acid content below 5% was obtained using a 3% Pd/aminopolysiloxane catalyst[72] or a 2% Pd/C catalyst[73]. The higher abundance of $H_2$ on the catalyst surface was claimed to be the main reason for the lower production of *trans* species.[74] However, the fast reaction rate in the supercritical conditions could lead to the formation of saturated FAMEs. The use of a novel support may also be helpful for reduction in the *cis*-*trans* isomerization on the Pd surface. A recent study reported that Pd nanoparticles in imidazolium-based ionic liquid showed higher hydrogenation activity than a conventional Pd/C catalyst and could selectively hydrogenate the FAMEs derived from soybean oil into *cis*-isomer monoene product to a higher extent.[75] The obtained product from the partially hydrogenated biodiesel was found to be more stable than the crude without compromising its cold-flow properties.

The exact reason for the high selectivity of the catalyst is not clear, but it seems to be related to the interaction between Pd and the support, as well as the dispersion of Pd.

The support was reported to have minor influence on the activity and selectivity of supported Pd catalysts towards hydrogenation of sunflower oil.[76,77] However, the pore structure of the support has an obvious effect on the catalytic performance of a supported metal catalyst towards partial hydrogenation. Pérez-Cadenas et al. reported that there was a strong interplay between the properties of the carbon coated on monoliths and the catalytic performance of Pd in selective hydrogenation of edible oils.[78,79] The authors further demonstrated that transport resistance effects had a strong influence on the activity and selectivity of Pd supported on a composite carbon layer/cordierite monolith support.[80] For partial hydrogenation of FAME, the selectivity was found to depend on whether Pd deposition was isolated to the outer carbon layer or whether Pd was deposited in both the carbon layer and through the cordierite monolith walls. In this case, the shorter diffusion path length with Pd isolated to the carbon layer was less favorable for *trans* product formation. Recently, Numwong et al. studied the effect of $SiO_2$ pore size (2-68 nm) on the catalytic performance of supported Pd toward partial hydrogenation of FAMEs derived from rapeseed oil.[81] Highest hydrogenation activity was achieved on Pd supported on $SiO_2$ with a pore size of 45 nm and the selectivity towards *cis*-monounsaturated FAME was found to be higher than those of two other catalysts with average pore sizes of 2 and 68 nm. The higher selectivity towards *cis* product for the Pd on supports with macropores was ascribed to the better accessibility of $H_2$ to Pd located in the relatively large pores. This is in agreement with the conclusion derived from the catalytic hydrogenation of FAME on Pd/C under supercritical conditions of propane.

More $H_2$ available on the metal surface will result in less formation of *trans* species in the hydrogenation process. In addition, the presence of an optimized pore size may, in addition to $H_2$ accessibility, arise because of the balance between surface area and Pd dispersion.

The catalytic performance of Pt towards partial hydrogenation of FAMEs was also found to be related to the structural characteristics of the support used in the catalyst. Philippaerts et al. investigated the activity and selectivity of Pt supported ZSM-5 towards the hydrogenation of methl elaidate.[82,83] After testing the samples obtained at different conditions, they claimed that a high dispersion of Pt on the support was crucial to achieve a selective hydrogenation of methyl elaidate (*trans*) in the presence of methyl oleate (*cis*). Also it was found that the microporous ZSM-5 support was more selective for hydrogenation of the slimmer *trans*- rather than *cis*-fatty acid compared to a larger pore $\gamma$-$Al_2O_3$ support due to shape-selectivity effects.[83] Thus, the availability of Pt sites for the reactants was proposed to be a key point for understanding the variation of activity and selectivity. From the presented results, it can be concluded that the pore structure of the support is crucial for the dispersion and availability of a metal, as well as accessibility of the substrate, which determine the contact time between the reactants and the active sites and hence has an effect on the catalytic performance of the catalyst towards partial hydrogenation of FAMEs. The interaction between metal and support appears to be less important but not well investigated. A quantitative measure of the number and strength of acidic/basic sites is needed to investigate the effect of the interaction between the metal and the support in partial hydrogenation.

### 2.1.2. Reaction mechanisms

Besides catalyst composition, another desirable aspect in catalysis is to reach an understanding of reaction mechanisms, which can be used to find correlations between systems not otherwise obviously related and to provide help in designing cost-effective catalyst with a desirable selectivity. In the case of C=C hydrogenation in heterogeneous catalysis, a well-known explanation is the Horiuti-Polanyi mechanism which assumes the incorporation of two hydrogen atoms into C=C in a sequential way, namely, via an alkyl surface intermediate first from the adsorbed olefin and one hydrogen, and then the corresponding alkane by incorporation of a second proton into the intermediate. In some cases, this mechanism can successfully describe C=C hydrogenation.[84-86] However, the Horiuti-Polanyi pathway was derived from C=C hydrogenation in olefins rather than FAME. It is still uncertain whether this mechanism can be extended to hydrogenation of C=C in FAMEs which contain several functional groups. Despite this fact, the reaction mechanism for hydrogenation of fatty acids based on the Horiuti-Polanyi mechanism was proposed.[87] As shown in Fig. 4a, the hydrogenation of C=C in a monounsaturated fatty acid occurs in two steps with the presence of a hydrogenated intermediate which can isomerize, or add an additional hydrogen atom. The step involving the addition of the first H is reversible and produces a double bond with potentially altered position or geometry, while the addition of a second H is irreversible and hence generates a saturated bond. The rate-determining step was considered to be the formation of the hydrogenated intermediate, depending on the hydrogen concentration.[88] For the fatty acids containing two C=C bonds, the C=C hydrogenation is suggested to proceed in a consecutive way, as shown in Fig. 4b. According to the proposed reaction pathway from the Horiuti-Polanyi mechanism, isomerization is favored over saturation at low hydrogen concentrations, allowing control of the product composition by changing the reaction conditions such as hydrogen pressure, agitation, and reaction time. This model seems to be consistent with the conclusion derived from the above experimental results that the availability of $H_2$ on the active sites of heterogeneous catalysts (supported Pd or Pt) determines the selectivity to *cis*-product during the partial hydrogenation process. However, there are still many uncertainties remaining about the reaction mechanism of C=C hydrogenation on solid catalysts. Some key points, such as adsorption mode, proton exchange, and rate-limiting step, are still needed to be further studied. In particular, FAME hydrogenation is supposed to be operated in a liquid environment, where there may be the presence of liquid bridges and cohesive forces between particles. In this case, the extension of the Horiuti-Polanyi mechanism to FAME hydrogenation requires deeper investigations. As pointed out by Zaera,[89] even C=C hydrogenation of olefins may be more complex than what is suggested by the Horiuti-Polanyi mechanism.

## 2.2. C=O hydrogenation

### 2.2.1. Catalyst

Hydrogenation of C=O in FAMEs has also attracted considerable attention since the products (natural fatty alcohols) are important raw compounds in many fields and methanol can be recycled for the transesterification process. In the edible oils and fats industry, the formation of *trans* products is not desirable during the process of C=O hydrogenation due to dietary reasons rather than lowering the melting point. Besides the isomerization reaction, the transesterification between the reactant and the generated fatty alcohols to form heavy esters is another side reaction and should be avoided. The catalytic hydrogenation of esters used in industry has been reviewed with focus on technical processes.[6,90] Commercial hydrogenation of esters into fatty alcohols has usually been carried out over a copper chromite catalyst under high hydrogen pressures (25-30 MPa) and reaction temperature in the range of 200-300 $^{o}$C.[91-93] These critical conditions with higher reaction temperature and higher $H_2$ pressure indicate the greater difficulty to carry out this reaction as compared to the partial C=C hydrogenation. The choice of copper chromites in industrial production was based on its stability rather than its higher activity for C=O hydrogenation. However, the toxic nature of Cr in the catalyst makes it unsuitable for wide applications. Thus, the development of a highly active catalytic system with good stability is an important topic in this field.

For hydrogenation of the C=O group in methyl esters, homogeneously catalyzed transfer hydrogenation has become a powerful tool and a wide range of unsaturated substrates can be employed.[94-96] Recently several homogeneous catalysts containing transition metals have been reported to be active for this reaction.[44,97-99] The osmium dimer homogeneous catalyst mentioned above was not only active for C=C hydrogenation but also efficient for production of fatty alcohols directly from olive oil under moderate operating conditions.[44] A homogeneous ruthenium complex catalyst was demonstrated to work efficiently for reduction of aliphatic and aromatic carboxylic esters into the corresponding alcohols at 100 $^{o}$C and hydrogen pressure of 50 bar.[99] The C=O hydrogenation on a homogeneous catalyst depended on the reaction temperature, substrate concentration, and solvent used in the process, while the hydrogen pressure in the range of 0.6-2.5 MPa has a minor effect on the hydrogenation reaction.[97] Obviously, homogeneous catalysts exhibit satisfactory activity and selectivity as well as moderate working conditions. Because of the already mentioned problems with recovery and regeneration of homogeneous catalysts, our focus is here on heterogeneous catalysts.

Metal catalysts based on group VIII metals have been investigated for C=O hydrogenation at different conditions. However, the noble metal Pd which was reported to be the most active metal for partial hydrogenation did not show detectable activity towards C=O hydrogenation when supported on $Al_2O_3$. However, the replacement of $Al_2O_3$ by ZnO was found to considerably improve the reaction rate of C=O hydrogenation on the Pd surface.[100,101] Various characterizations indicated that the formation of Pd-Zn intermetallic species with new sites for the selective adsorption of C=O may be responsible for the improved activity of Pd towards C=O hydrogenation. The choice of suitable oxide promoter appears to play a key role in C=O activation on metal supported catalyst.[102] Besides oxide promoter, modification of Pd by another metal can also improve its activity towards C=O hydrogenation. For instance, diatomite supported bimetallics Pd-M (M = Cu, Co, Ni) have been demonstrated to be active for hydrogenation of long-chain aliphatic esters, including methyl palmitate, methyl stearate, and methyl laurate.[103] The good performance of the binary metal systems for the selective hydrogenation of long-chain fatty esters towards corresponding alcohols may be related to the ligand effect between Pd and M, as well as metal-support interactions.

An interesting type of catalyst studied by different groups is alumina supported tin-containing catalysts. Narasimhan et al. reported that Ru-Sn-B supported on $Al_2O_3$ could selectively hydrogenate methyl oleate into oleyl alcohol under a hydrogen pressure of 4.5 MPa at 270 $^{o}$C.[104-106] The selectivity of the transfer from ester to alcohol was about 80% with 80% conversion of the ester. The active sites were proposed to be the Ru particles in interaction with tin oxide acting as Lewis acid centers involved in the activation of the carbonyl group.[106] Boride was claimed to be essential in this catalyst towards hydrogenation of methyl oleate into oleyl alcohol, although the role of boride was not clarified. In order to understand this, Pouilloux et al. studied the hydrogenation of methyl oleate into oleyl alcohol on the $Ru/Al_2O_3$ catalysts modified with Sn or B species.[107] It was found that the presence of B resulted in improvement of the selectivity towards saturated esters, while the addition of Sn to the $Ru/Al_2O_3$ catalyst significantly improved the production of unsaturated alcohol with a selectivity of about 50%. The relatively lower selectivity was ascribed to the rapid side reaction between methyl oleate and oleyl alcohol leading to the formation of heavy esters (oleyl oleate). These results indicate that it is not B but primarily Sn which acts as the promoter in hydrogenation of FAME into fatty alcohol. The performance of the RuSn system without B species towards C=O hydrogenation was further improved by optimization of the preparation method. Cheah et al. synthesized the catalysts without B using different techniques, including sol-gel, impregnation, and co-precipitation.[108] After optimization of the preparation procedures and the atomic ratio of Ru to Sn, the catalyst without B also exhibited good performance towards oleic acid hydrogenation into fatty alcohol with a selectivity of 97% at a conversion of 81.3%. Recent studies of the effect of the preparation method on activity of Ru-Sn-B catalysts further confirmed that it is the interaction between Ru and Sn, as well as the removal of chlorine in the catalyst, rather than the presence of B, which is responsible for the C=O hydrogenation activity.[109,110] Although the exact role of Sn is not clear, it was proposed that Sn in the catalyst might change the adsorption behavior of a catalyst system towards the substrate and increase the affinity for C=O groups on the catalyst surface.[108]

Nowadays the systems containing Sn supported on oxides are still of great interest in hydrogenation of methyl esters to fatty alcohols. The focus has been on evaluation of the effect of support, metal, and preparation methods involving different precursor sources. Miyake et al. tested hydrogenation of methyl laurate or methyl palmitate into the corresponding alcohols over Ru-Sn and Rh-Sn supported on $Al_2O_3$, $SiO_2$, and $ZrO_2$ at 300 $^oC$.[111] It was found that the support with a relatively low surface area was favorable for selective hydrogenation of the methyl esters into alcohols. The esterification reaction between the raw methyl ester and the produced alcohol was also observed and could proceed under the reaction conditions even without the catalysts. The activity order, as well as the selectivity to alcohol, for different metals with Sn supported on $\gamma$-$Al_2O_3$ was as follows Rh > Pt > Ir > Ru > Pd, which seems to follow the Sabatier principle except for Pd. Modifying the electronic properties of a noble metal by introduction of a suitable third metal may also change the activity of the monometallic-Sn system towards C=O hydrogenation. For example, the addition of Pt to Ru-Sn/$Al_2O_3$ catalysts was found to improve the activity and selectivity of the catalyst towards methyl laurate hydrogenation.[112] Interestingly, the addition of Pt to the Ru-Sn/$Al_2O_3$ catalyst not only modified Ru but increased the reducibility of $SnO_2$. After reduction of the catalyst by $H_2$, a $RuSn_x$ alloy was easily formed and reduced the dissolution of Sn species during the hydrogenation reaction and thus enhanced the stability of the catalyst. The metal precursors for preparation of the Ru-Sn/$Al_2O_3$ were also found to have an effect on its performance towards methyl oleate hydrogenation.[113] The selectivity towards unsaturated alcohols was observed to be higher on the catalyst prepared from chlorine-free precursors than on the catalyst prepared from metal chlorides. It was proposed that the residual chlorine on the catalyst surface poisoned the active sites and hampered an effective interaction between Ru and Sn species. When the catalyst precursor from metal chlorides was reduced by $NaBH_4$, the selectivity towards alcohol was improved due to removal of residual chlorine by the reducing agent and a higher dispersion of the obtained Ru-Sn species. Based on the above results, it can be concluded that the effect of support and metal precursor on selectivity can be related to the dispersion of metal and metal-support interaction.

In order to reduce the cost of the hydrogenation catalyst, samples without noble metals were also investigated for C=O hydrogenation. Yuan et al. studied a Cu-Zn/$Al_2O_3$ catalyst for hydrogenation of palm oil esters to alcohols.[114] For comparison, the commercially available CuCr, CuCrBa, and CuCrMn catalysts were also tested for the production of alcohols. The results showed that the CuZn catalyst gave a higher yield for alcohols than the other samples under the same reaction conditions. However, the conversions of palm oils were not reported and the stability of the Cu-Zn/$Al_2O_3$ catalyst compared to the CuCr system was not studied. Pouilloux et al. investigated CoSn supported on $Al_2O_3$ or ZnO towards hydrogenation of methyl oleate into oleyl alcohol at 270 $^{o}$C and 8.0 MPa.[115-117] It was found that saturated esters could be produced from methyl esters over the Co particles without $SnO_x$. Furthermore, the Co/$SnO_x$ atomic ratio was suggested to determine the selectivity to unsaturated alcohols or heavy esters.[116] The maximum selectivity to oleyl oleate was about 70% at the methyl oleate conversion of 80%. Comparison of the activities and the selectivities between CoSn and RuSn showed the hydrogenation rate on Co was lower than that on Ru and the side transesterification reaction between methyl oleate and oleyl alcohol was more serious on the CoSn catalyst.

### 2.2.2. Reaction mechanisms

For the heterogeneous catalysts towards C=O hydrogenation, many studies have been focused on correlation of the catalyst structure with the observed activity for FAME hydrogenation. In the case of RuSn supported on $Al_2O_3$, these studies have led to a basic agreement about the surface state and the role of Ru and Sn for the C=O hydrogenation. Hydrogen is proposed to be bound to Ru sites to form metal hydride, while the C=O bond in the ester is activated by the Lewis acid sites ($Sn^{2+}$ or $Sn^{4+}$). The activity and the selectivity of the RuSn system towards hydrogenation of FAMEs into alcohols depend on the interaction between metallic Ru and acidic Lewis ($Sn^{2+}$ or $Sn^{4+}$) sites via oxygen.[106] To achieve a high activity, the interaction between Ru and Sn must be favorable for hydrogen transfer from the RuH hydride to the C=O group attached to the Lewis acid sites. Pouilloux et al. visualized several states of Ru and Sn on the catalyst surface.[118] As shown in Fig. 5, Ru and $SnO_x$ were dispersed without mutual interaction at low concentration of Sn, and $SnO_x$ might decorate Ru particles with increasing Sn content in the catalyst. Finally, Sn would cover the surface and reduce active sites for the hydrogenation reaction when the Sn content reached a relatively high level. The different phases of Sn and Ru were proposed to correlate to the activities of the catalysts at the different molar ratio of Ru to Sn.

Although an agreement exists concerning the roles of Ru and Sn, there are different opinions on the nature of intermediate species formed during the hydrogenation process. Deshpande et al. proposed a reaction pathway involving aldehyde as the intermediate,[106] as shown in Scheme 1. In this pathway, the initial hydride (RuH) attacks the ester group in the adsorbed reactant and forms an unstable carbanion, which produces aldehyde and then the final alcohol. It was also suggested that boron species could interact with ruthenium which would favor the specific activation of the hydrogen in hydride form. This reaction mechanism could be further confirmed if the intermediate aldehyde could be detected during the hydrogenation reaction. However, the aldehyde was not detected in the kinetic study and the authors ascribed it to the fast hydrogenation of the aldehyde into alcohol at the high pressure of $H_2$. Pouilloux et al. proposed a reaction mechanism for the hydrogenation of methyl oleate into oleyl alcohol based on various experimental results.[118] The proposed elementary chemical steps for methyl oleate hydrogenation are shown Scheme 2. Metallic Ru activates hydrogen into hydride directly and $SnO_x$ acts as an adsorption site for methyl oleate adsorption through the C=O bond. Then the H on Ru attacks the carbon atom of the carbonyl group to obtain a hemiacetal, which is converted to alcohol under high hydrogen pressure. A similar reaction pathway was also proposed for production of fatty alcohol over CuCr systems.[119] It can be seen from this reaction mechanism that the alcohol is formed directly from the hemiacetal adsorbed on the catalyst surface without the intermediate formation of aldehyde. The exact surface intermediates during C=O hydrogenation on the metal surface require further experimental and theoretical studies.

## 2.3. *Cis-trans* isomerization

During the hydrogenation of C=C or C=O bonds in FAMEs, the *cis-trans* isomerization is not desirable and should be minimized. However, the conversion from *cis* to *trans* is thermodynamically favorable since the latter species is more stable. The molar ratio of *cis*- to *trans*- at an equilibrium state can be roughly calculated according to the expression: [*cis*]/[*trans*]=exp(-Δ*H*/RT), where Δ*H* is the enthalpy difference between the two species. For C18:1 fatty acid the enthalpy difference is about 3.85 kJ/mol,[69] whereas the average value for the two species in vegetable oils has been determined to be about 4.10 kJ/mol.[21] Thus, at an equilibrium state the *trans* content is estimated to be in the range of 70-79% at 100-300 °C. This indicates that the *trans* form should be dominant from a thermodynamic viewpoint. The only way to control the isomerization is to change the kinetics of isomerization on a catalyst surface. Thus, many studies have focused on understanding the kinetics of isomerization in order to decrease the formation of *trans* products.

Direct measurement of isolated isomerization reaction is, however, difficult since hydrogenation and isomerization are parallel reactions in the hydrogenation process. The traditional method to study isomerization has been a statistical analysis of the overall kinetic rate equation derived from elementary steps containing hydrogenation and isomerization.[120-123] Jonker et al. studied the kinetics of hydrogenation and isomerization of methyl oleate and elaidate on a supported nickel catalyst using the Horiuti-Polanyi mechanism which involves a partially-hydrogenated surface intermediate on the catalyst.[55] The activation energies for *cis* and *tran* hydrogenation were calculated to be 32.2 and 28.1 kJ/mol, respectively, while the activation energy for isomerization was 47.2 kJ/mol. These activation energies indicate that the hydrogenation rates of *trans* and *cis* isomers should be close to each other, while the isomerization reaction should be more difficult than the hydrogenation on the Ni surface. This is in agreement with experimental observations where the rates were equal for hydrogenation of *trans* or *cis* isomers.[124] A similar trend was also obtained in a kinetic study of soybean oil hydrogenation on Ni/$Al_2O_3$, except that the values of the three activation energies were higher, e.g. 68 kJ/mol for the partial hydrogenation and 72 kJ/mol for the isomerization reaction.[56] These results confirm the possibility that isomerization is thermodynamically favorable but can be kinetically controlled during the process of FAME hydrogenation on some metal surfaces.

In order to compare the activities of noble metals towards isomerization, Deliy et al. studied the kinetics of methyl oleate hydrogenation and *cis*-*trans* isomerization on carbon supported noble metals (Pd, Ru, Rh, Pt, Ir) in the temperature range of 25-100 $^{o}$C and hydrogen pressure from 1 to 10 bar.[125] Both the *cis*-*trans* isomerization and the hydrogenation reaction were assumed to proceed on all the studied metals. However, the activities of the metals for the isomerization were different: the second-row metals (Rh, Ru, Pd) displayed relatively high activities in the isomerization reaction, while Pt and Ir showed minor activity for this reaction. It was proposed that this might be understood from the adsorption strength and adsorption mode of olefins on these metals. An additional, interesting result is that the Pt/C catalyst not only showed minor activity for the isomerization but had the highest catalytic activity towards the *cis*-methyl oleate hydrogenation. A lower formation of *trans* species on Pt than Pd and Ni was also reported during the hydrogenation of sunflower oil.[126] This indicates that Pt is a promising candidate as a catalyst for partial hydrogenation of FAMEs with minimal isomerization.

Besides the active metal phase, the support may also affect the *cis*-*trans* isomerization during the hydrogenation process. For instance, a slightly lower *trans* formation was observed for Cu supported on $Al_2O_3$ than $SiO_2$.[62] Diffusion resistance effects due to the pore structure of carbon, varying diffusion path length of the support as well as shape selectivity were also demonstrated to affect the selective formation or hydrogenation of *trans* species,[76-80,83] as summarized in section 2.1.1. However, the further discussion of support effect on isomerization selectivity must consider hydrogenation. This is reasonable since isomerization and hydrogenation reactions are parallel and interdependent. Kinetic studies also confirmed that the ratio of *cis/trans* methyl oleate isomers was correlated to the relative reaction rates of hydrogenation and isomerization.[123] This may be understood from the Horiuti-Polanyi mechanism. According to the reaction mechanism in section 2.1.2, the isomerization may occur when a hydrogenated intermediate is formed. De-protonation of the intermediate would compete with the further hydrogenation. If there are enough protons on the catalyst surface, the intermediate hydrogenation is expected to have a faster reaction rate than the de-protonation which may lead to the formation of *trans* species. Therefore, it can be concluded that the support also affects the isomerization in an indirect way probably through changing the metal dispersion which is considered to be related to hydrogenation.

The kinetic study seems to be a suitable way to investigate the isomerization reaction. However, it should be noted that the kinetics are strongly related to the model used in the study. All the kinetic expressions discussed here were derived from the classical LHHW model based on non-competitive adsorption. This contradicts the traditional viewpoint that the competitive adsorption is more universal in most cases. A true model derived from a verifiable reaction mechanism containing the elementary steps should be more accurate to evaluate the isomerization selectivity on a catalyst surface.

## 2.4. DFT studies

First principles calculations based on the density functional theory (DFT) have grown into a popular and versatile method to rationalize experimental results in heterogeneous catalysis.[127-131]

The broadest definition of FAME produced from vegetable oils and animal fats includes all chain lengths, but most natural fatty acids contain the number of C in the range of 4-22 with C18 being most common. However, calculations of catalytic hydrogenation of unsaturated FAMEs with more than four carbon atoms have not yet been reported. Thus, we have here chosen to review some typical DFT studies concerning hydrogenation of C=C and C=O in aldehyde or organic acids. Hopefully this can shed light on the understanding of FAME hydrogenation.

Loffreda et al. used first-principles calculations to investigate the elementary steps and to build a possible kinetic model to understand the hydrogenation of C=C and C=O in acrolein ($CH_2CHCHO$) on Pt(111) surface.[132] It was found that the selectivity, e.g. C=C and C=O hydrogenation depended on the balance between the hydrogenation reactions on the surface and the desorption steps of the partially hydrogenated products. After analysis of the kinetic model, it was concluded that the desorption energy of the product seemed to be the key parameter for the hydrogenation selectivity. Pallassana and Neurock studied the reaction pathways for acetic acid dissociation on Pd(111) with the presence of excess surface hydrogen.[133] It was found that H atoms on the Pd surface were not likely to react with the oxygen in the carbonyl group of acetic acid but rather with the C-OH, since the latter is more energetically favorable.

A recent detailed DFT study of methyl propanoate hydrodeoxygenation was reported by Dupont et al.[134] In their study, the hydrogenation of propanal into propanol was performed on the surfaces of NiMoS and $MoS_2$ catalysts, which were demonstrated to be active in hydrodesulfurization and hydrodeoxygenation.[135,136] In the DFT computation, two reaction pathways for propanal hydrogenation starting from the coadsorbed state between propanal and dissociated hydrogen were studied. As shown in Fig. 6, both the proposed propoxy route and the hydroxylpropyl pathway are exothermic and favorable from a thermodynamic point of view. However, the propoxy route involving first CH and then OH formation requires relatively lower activation energy barriers. Similar results were obtained for propanal hydrogenation on $MoS_2$ but the activation energy barriers of the above two steps were found to be higher. It was proposed that the higher ability for propanal hydrogenation on NiMoS than $MoS_2$ can be ascribed to the special configuration of propanal on the NiMoS surface through the carbonyl group on the Ni-Mo mixed site.

There are also several studies about the activation of carboxylic esters, such as methyl acetate.[137,138] From these DFT calculations, it can be further confirmed that the reactivities of C=O and C=C should be different and may proceed selectively on different catalysts. The adsorption configurations of the reactants, as well as the desorption of products, seem to be important factors to control the selectivity of hydrogenation reactions.

The above DFT studies are attractive in understanding hydrogenation of C=C or C=O groups. However, it should be kept in mind that the model molecules used in the studies are not unsaturated FAMEs which have different functional groups from the above molecules. It is expected that FAME hydrogenation should be different since FAME has different functional groups, e.g., C=C, C=O and O=C-O. It is still not known how extensive the differences can be. Thus, a predictive vision from the above results is still difficult now and one cannot further extend these findings to FAME hydrogenation.

Again biodiesel mainly consists of methyl ester with C18 molecule being most common. The computational requirements for such a large and complex system are vast due to the many plausible adsorption modes. And it would be more complicated if intermolecular interactions are considered. There might be some solutions for this problem. For instance, Salciccioli et al. used DFT calculations to systematically study the geometric and energetic trends of adsorbed carboxylic acid and ester intermediates on Pt(111),[139] and then proposed a group additivity scheme which was used as a tool to parameterize and screen large oxygenate reaction mechanisms for identification of important reaction steps. This could be a way to reduce the computation time for modeling hydrogenation of long-chain FAMEs. Another possible way forward is to start from a small FAME molecule such as methyl crotonate and then extend the results from small to large FAME molecules based on combined experimental and theoretical studies. However, the hydrogenation of small FAME molecules is not studied. Future experimental work focusing on understanding the hydrogenation of small FAME molecules may be needed to foster theoretical advances. It can be expected that the investigation of unsaturated methyl ester hydrogenation with DFT calculations will further clarify the observed differences in various catalysts. This would greatly improve the understanding of the reaction mechanisms and in the future aid rational design of cost-effective catalysts for hydrogenation reactions.

## 3. Reactor configuration

Generally, the reactor used for hydrogenation reactions can be divided into two types: batch and flow reactors. Numwong et al. found that the type of reactor had an effect on the catalytic performance of Pd towards partial hydrogenation of polyunsaturated FAMEs.[140] Partial hydrogenation carried out in a continuous flow reactor had a reaction rate 4-5 times higher than that in a batch reactor. However, the selectivity towards monounsaturated FAME is higher at a high conversion of polyunsaturated FAME in the batch-type reactor. Differences in contact between oil and catalyst surface were proposed to explain the experimental results. The different performance between flow and batch reactor motivated us to review the general aspects of interesting reactor configurations for FAME hydrogenation.

### 3.1. Flow reactor

Catalytic hydrogenation under industrial conditions is usually operated in a tubular plug-flow reactor packed with a supported catalyst. In a flow reactor, the reactants can be in the form of gas or liquid phase. Since FAMEs always have relatively high boiling points, significant amounts of energy are required to vaporize them from liquid phase to gas phase. Furthermore, the gas-phase hydrogenation can only be operated at low concentrations of FAMEs, resulting in low throughput with respect to the reactor volume. Hence, FAME hydrogenation is normally carried out in liquid-phase. In this case, the unit containing three phases, e.g. solid catalyst, liquid FAME, and gas-phase $H_2$, is called a trickle bed reactor.

Actually, trickle-bed flow reactors represent one of the widely used industrial reactors for carrying out chemical processes involving solid-catalyzed reactions with gas and liquid phase reactants. The industrial hydrogenation of methyl esters into fatty alcohols is operated in a trickle-bed flow reactor with Cu-based pelletized catalysts. According to the flow directions of gas and liquid phase reactants, the flow reactor packed with a fixed bed of catalyst can be classified as co-current or counter-current trickle-bed reactor, as shown in Fig. 7. The choice of operation mode can be based on rational considerations of the limiting reactant under the operating conditions. For instance, if liquid is assumed to be the limiting factor, the focus for design of the trickle bed reactor should be on improvement of wetting efficiency and particle-liquid mass transfer rate. In the case of gas-limited reactions, the mass transfer resistance contributed from the liquid phase should be reduced while maintaining a good liquid distribution and avoiding the formation of hot spot. In most industrial operations, the counter-current operation mode is more preferable due to simple design, low pressure drop (compared to liquid full operation), reasonable heat transfer efficiency, and convenience of controlling temperature. However, there is no general guidance for FAME hydrogenation as to which flow configuration will perform better since the properties of FAMEs vary with the starting sources. For a specific reaction system, the effect of operation conditions, e.g., flow direction, temperature, and flow rate, on the performance of a reactor should be investigated extensively to evaluate the interplay of various factors before choosing a flow mode for a large-scale pilot. Some guidelines for designing experiments in a trickle-bed reactor are available in some references.[141,142]

Besides the reactor design, another possibility to reduce mass transfer resistance in a trickle-bed reactor is the use of structured catalysts compared to the traditional packed solid catalyst. For instance, monolithic catalyst supports which are not sensitive to the pressure drop in the trickle-bed reactor can be operated using relatively thin washcoat layers of catalyst on the monolith catalyst. This would increase the catalyst external surface area contacted with reactants and hence reduce the diffusion distance. In addition operation with a gas-liquid flow ratio providing the so called Taylor or slug-flow regime is favorable for a process mass transfer limited in the gas phase reactant. Comparison between a monolith and a packed-bed catalyst operated in pilot-scale experiments showed the superiority of the monolith catalyst over the other one in terms of mass transfer and the hydrogenation selectivity due to a narrower residence time distribution.[143] More information about structured catalysts and reactors are available elsewhere.[144]

### 3.2. Batch/Slurry reactors

The batch reactor is another type of commonly used reactor for performing chemical reactions. Similar to the flow reactor, a main problem for hydrogenation reactions operated in a batch reactor is the diffusion resistance of gas-phase $H_2$ to reach the solid catalyst surface. A simple method is to provide mechanical agitation or a spinning basket in a pressurized slurry to accelerate the transport of $H_2$. In this case, the temperature control and the mass transfer should be more favorable than in a regular flow reactor. However, the efficiency of this technique is still too limited to achieve an obvious improvement on the production rate due to low solubility of $H_2$ in organics. For instance, the coefficients of the volumetric gas-liquid mass transfer and the liquid to solid mass transfer in a monolithic stirred reactor only increased about 5.6 and 1.6 times, respectively, when changing the agitation speed from 800 to 1400 rpm.[145]

In order to significantly increase the transport of $H_2$ from gas- to liquid-phase and then to the catalyst surface, an interesting method under investigation in a batch reactor is the supercritical-fluid technique. In a supercritical state of a solvent, distinct liquid and gas phases do not exist and hence gas can act like a liquid and easily reach the solid surface. The favorable solvent and transport properties of supercritical fluids make this technique an attractive alternative to the conventional industrial hydrogenation slurry reactors which suffer from gas-liquid mass transfer limitations. Under supercritical conditions of propane, the reaction rate after optimization was found to be more than 500 times higher than that in a traditional batch hydrogenation.[72] The hydrogenation of FAME into fatty alcohols was also suggested to be more favorable at supercritical conditions than the traditional industrial batch processes. It was reported that the hydrogenation rate of a long chain FAME to the corresponding alcohol under propane supercritical conditions could be promoted 5-10 times compared to the batch reactor operated under two phases and even be comparable to that of gas-phase hydrogenation of smaller molecules.[146] Besides the greatly improved reaction rate, another characteristic of the hydrogenation of FAMEs in a supercritical state is the reduction of the *trans* fatty acid content in the product. For partial hydrogenation of methylated rapeseed oil, the *trans* content was dramatically reduced to be about 3.8% under supercritical conditions of propane.[72] The reduction in the formation of *trans* acid and stearic acid was also observed in hydrogenation of sunflower oil on Pd/C in supercritical propane.[147]

The commonly used supercritical fluids for FAME hydrogenation are $CO_2$, propane, and butane. For the hydrogenation of FAME, several fluids, e.g. $CO_2$, propane, butane, and dimethylether (DME), have been investigated in a batch reactor.[146-152] The choice of solvent medium has an obvious effect on the product selectivity of FAME hydrogenation. Andersson et al. studied the hydrogenation of FAMEs derived from soybean oil using $CO_2$ or propane as solvent and found that the hydrogenation reaction rates were faster under propane atmosphere but along with higher selectivity to saturated alkanes.[148] Supercritical DME for vegetable fat hydrogenation was reported to improve the melting profile of the hydrogenated products compared to that with supercritical propane.[153] However, the over hydrogenation of FAME on Ni-based catalysts was not observed in other studies using propane as the solvent. It may indicate that the hydrogenation reactions involved under supercritical conditions can be controlled through the catalyst used and by the operating conditions. Furthermore, recent modeling of the hydrogenation process for fatty oil hydrogenation with supercritical solvent has shown that the use of a co-solvent (binary fluids) in a supercritical technique may reduce the risk of explosion during the operation.[154]

To ensure the operation under a supercritical condition, if propane is assumed to be the solvent, the $H_2$ concentration can be freely chosen while the FAME concentration in the reaction mixture is limited to less than 1 mol%.[149] Otherwise, the mass transport limitations would prevail in the process and hence affect the reaction rate, selectivity, and time to achieve a certain conversion. Hark and Härröd ascribed the loss in reaction rate at high substrate concentrations to a split of the supercritical reaction mixture into two different phases (substrate- and $H_2$-rich phase).[150] Brands et al. made a detailed analysis of various aspects, including thermodynamics, and process design, using supercritical butane.[155,156] The thermodynamic analysis showed that the substrate concentration can be increased to 2.5 mol% with an equilibrium conversion of 99.2%. But the increase in substrate concentration would result in higher reaction temperature, which would lead to a drop in selectivity due to the formation of alkanes.

Despite the significant improvement in $H_2$ transport to the catalyst surface in a supercritical fluid, avoidance of complete hydrogenation and an increase in substrate concentration are the two main issues hindering the adoption of this technique for industrial applications.

### 3.3. Membrane reactor

Another way to improve $H_2$ diffusion from gas-phase to catalyst surface is by the use of a membrane reactor. Membrane reactors generally offer advantages over conventional fixed bed reactors, such as higher energy efficiency and compact modular construction etc. In a typical membrane configuration, the catalyst is attached on one side of the membrane and the reactants with different phases flow separately on either side of the membrane. In this case, $H_2$ can reach the catalyst surface directly without a long diffusion through the liquid phase and hence diffusion resistance of $H_2$ may be reduced.[157] It is expected that the *cis*-*trans* isomerization can be reduced though the exact mechanism is not clear. Singh et al. demonstrated an integral-asymmetric metal-polymer composite catalytic membrane approach for hydrogenation of soybean oil with a low production of *trans* fatty acids.[158] Fig. 8 shows the schematic of the hydrogenation process with the membrane reactor. $H_2$ is fed into the reactor from the porous side of the membrane, while the oil is pumped and flowed over the Pt-sputtered side of the membrane. Interestingly, the production of *trans*-fatty acids was found to be relatively low in this membrane reactor. However, contrary to this finding, a study performed by Schmidt and Schomäcker demonstrated a negative impact of a membrane reactor.[159] They made a systematical study of partial hydrogenation of sunflower oil in a membrane reactor consisting of a porous α-$Al_2O_3$ membrane with Pd or Pt. The hydrogenation reactions were also tested in a slurry reactor, which was used as a reference to the membrane reactor. However, the authors did not find any improvement in selectivity for the desired product with the membrane pore-flow-through mode compared to the slurry reactor. The content of *trans* fatty acids (30-45%) in the product obtained in the membrane reactor was even higher than that (12%) produced in the slurry reactor.

The different experimental results observed in the above two membrane reactors should be not only related to the reactor configuration, but to the diffusion properties of the membrane. As demonstrated by Fritsch and Bengtson, the membrane prepared by the addition of ready-made supported catalyst to the casting solution had a low catalyst loading and showed a low activity in hydrogenation reactions.[160]

The membrane reactor appears to be a good alternative to the traditional flow/batch reactor since transport limitations can potentially be reduced and the operation is flexible. However, as pointed by Veldsink,[157] membrane reactors suffer from difficulties related to catalyst regeneration. The realization of membrane reactors for hydrogenation reactions in industry is strongly related to the development of membranes with the appropriate diffusion properties and catalysts with good stability and regenerability.

## 4. Conclusions and outlook

In summary, this review presents several aspects of catalytic selective hydrogenation of C=C and C=O in FAMEs, including catalysts, reaction mechanisms, and reactor configuration. The development of catalysts for FAME hydrogenation depends on the applications of the products. For partial hydrogenation of FAMEs, the mono-metals in the

VIII group are active in C=C hydrogenation under moderate operating conditions. The challenge mainly lies in avoiding or minimizing the selectivity to *trans*-FAMEs which have relatively high melting points. In this case, Pt seems to be a good candidate since it was found to be the least active metal towards isomerization. Future investigations can be dedicated to modify the Pt surface by formation of near-surface alloys with lower selectivity to the isomerization. As for the reduction of FAMEs into fatty alcohols, the operation conditions are more critical than those of partial hydrogenation. The catalytic hydrogenation of C=O in a FAME needs two different adsorption sites, a metallic center for $H_2$ adsorption and an electron-deficient center like $SnO_x$ for C=O activation. Note that due to the increasing demands of noble metals for various applications, the development of non-noble metal based catalysts towards selective hydrogenation is of considerable interest in this field.

Though many catalysts have been tested for FAME hydrogenation at different conditions, the reaction mechanism of FAME hydrogenation and the key reaction intermediates are still not clearly understood. For example, the prevalent consensus about FAMEs hydrogenation into fatty alcohols on $RuSnO_x/Al_2O_3$ is that the active site is provided by the synergy between Ru and the promoter $SnO_x$. Nevertheless, the nature of the active sites and interactions among active components, support, and promoter are still elusive. However, it is desirable to reach fundamental understanding and theoretical insights into the chemical process of FAME hydrogenation on catalyst surfaces to allow rational improvement of existing catalysts and design of novel cost-effective catalysts. The difficulty mainly lies in the fact that FAME hydrogenation is always operated in liquid phase and hence the traditional characterization techniques for gas-phase reactions are not appropriate to detect reaction intermediates in a liquid-phase reaction. A useful approach is to study the kinetics which describes the characteristic behaviors of the reactants on the catalyst with time under various reaction conditions, and then interpret the kinetic results on the basis of assumptions. Furthermore, isotope labeling using deuterium can be employed to obtain deeper insights into the catalytic hydrogenation. Besides experiments, theoretical models and simulations are also needed to quantify the influence of a proposed hydrogenation mechanism. A combination of surface science approaches with molecular simulations would bridge the gap between the macroscopic characteristics (e.g., kinetics) of practical catalysts and molecular understanding of hydrogenation reactions.

A challenge for hydrogenation reactions in liquid phase is the low solubility of $H_2$ in FAMEs and hence interfacial mass transport limitations. This may be solved by a reactor design, such as supercritical operation and membrane reactor. The supercritical fluid should be operated carefully in order to avoid the presence of over hydrogenation which is not desirable in the hydrogenation reaction network. Furthermore, there are several issues required to be sufficiently addressed, including the high thermal energy required to achieve supercritical conditions and improvement of substrate concentration. As for the membrane reactor, it appears to be an attractive concept for FAME hydrogenation, but a robust catalyst with good regenerability, as well as development of membranes, are required before commercial applications. Finally, it should be kept in mind that no matter the reactor configuration, the heat generated during the hydrogenation process must be removed or utilized in order to avoid hot-spot formation in a reactor.

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Scheme 1. The mechanism involving the major surface species on the RuSnB/$Al_2O_3$ catalyst. Adapted with permission from ref. [106].

Scheme 2. Mechanism of the direct hydrogenation of methyl oleate into unsaturated alcohol RuSn/$Al_2O_3$ catalyst. Adapted with permission from ref. [118].

Fig. 1. Possible chemical reactions involving hydrogenation of C=C and C=O in unsaturated FAMEs excluding isomerization, hydrodeoxygenation, decarbonylation, decarboxlation, and thermal decomposition.

Fig. 2. Fatty acid composition and oxidative stabilities of FAMEs hydrogenated from (a) fat from rendering plants and (b) used cooking oil. Reproduced with permission from ref. [20].

Fig. 3. Correlation between the activity order and the *d*-band center of the metal towards hydrogenation of natural oils.

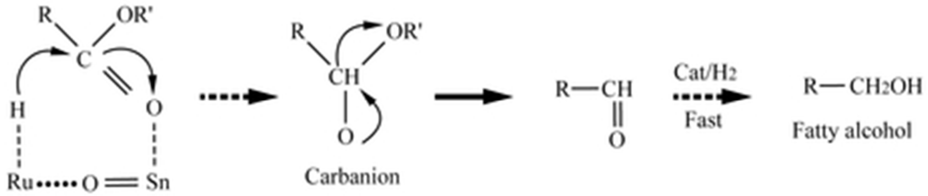
Fig. 4. Reaction pathways of hydrogenation of C=C in (a) monounsaturated and (b) diunsaturated fatty acid. D, M, S and * represent diene, monoene, saturate and potentially isomerized, respectively. Adapted with permission from ref. [87].

Fig. 5. Model representating the RuSn centers with different tin contents: (1) Sn/Ru<4; (2) 4<Sn/Ru<5.5; (3) Sn/Ru>5.5. Adapted with permission from ref. [118].

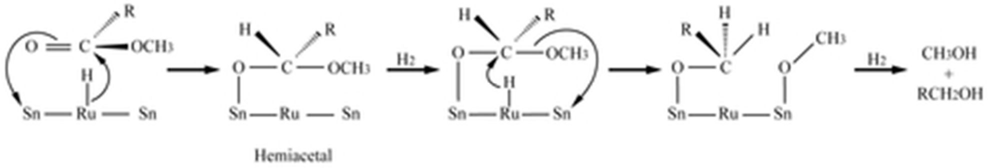
Fig. 6. The two possible hydrogenation pathways of propanal on NiMoS: the propoxy route with first CH and then OH formation (black); the hydroxylpropl with first OH and then CH (green). The most stable coadsorption state between propanal and two hydrogen atoms is taken as reference. Energies are reported in eV. Reproduced with permission from ref. [134].

Fig. 7. Operating modes of fixed-bed multiphase catalytic reactors.

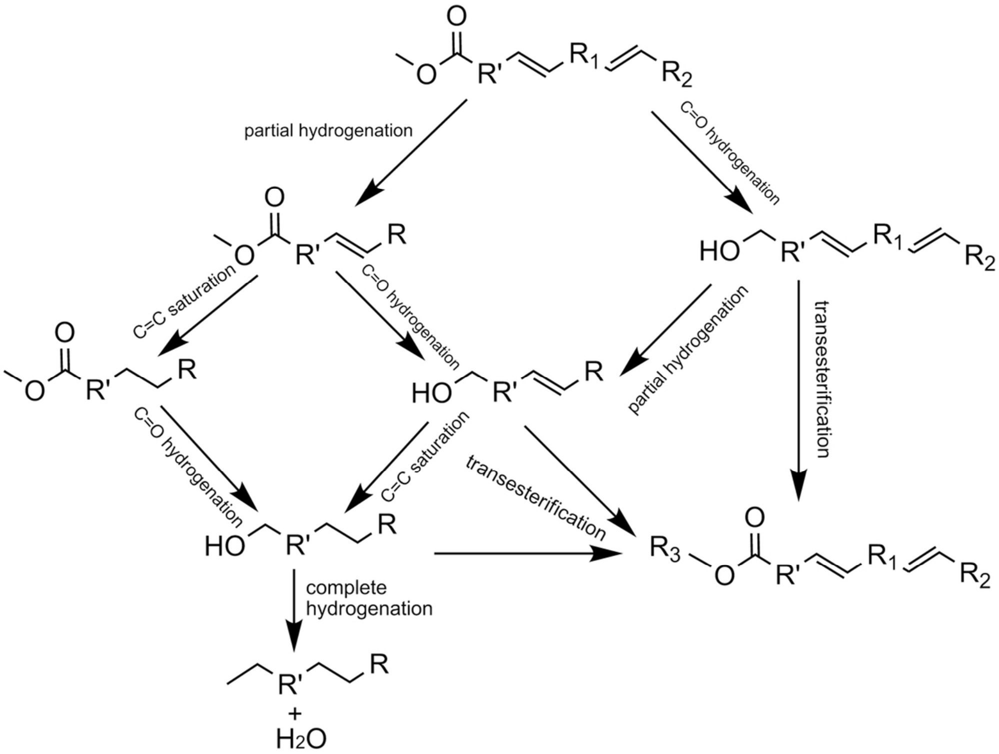
Fig. 8. Schematic of vegetable oil hydrogenation as it would take place in the catalytic membrane reactor. PEI represents the poly-ether-imide. Reproduced with permission from ref. [158].



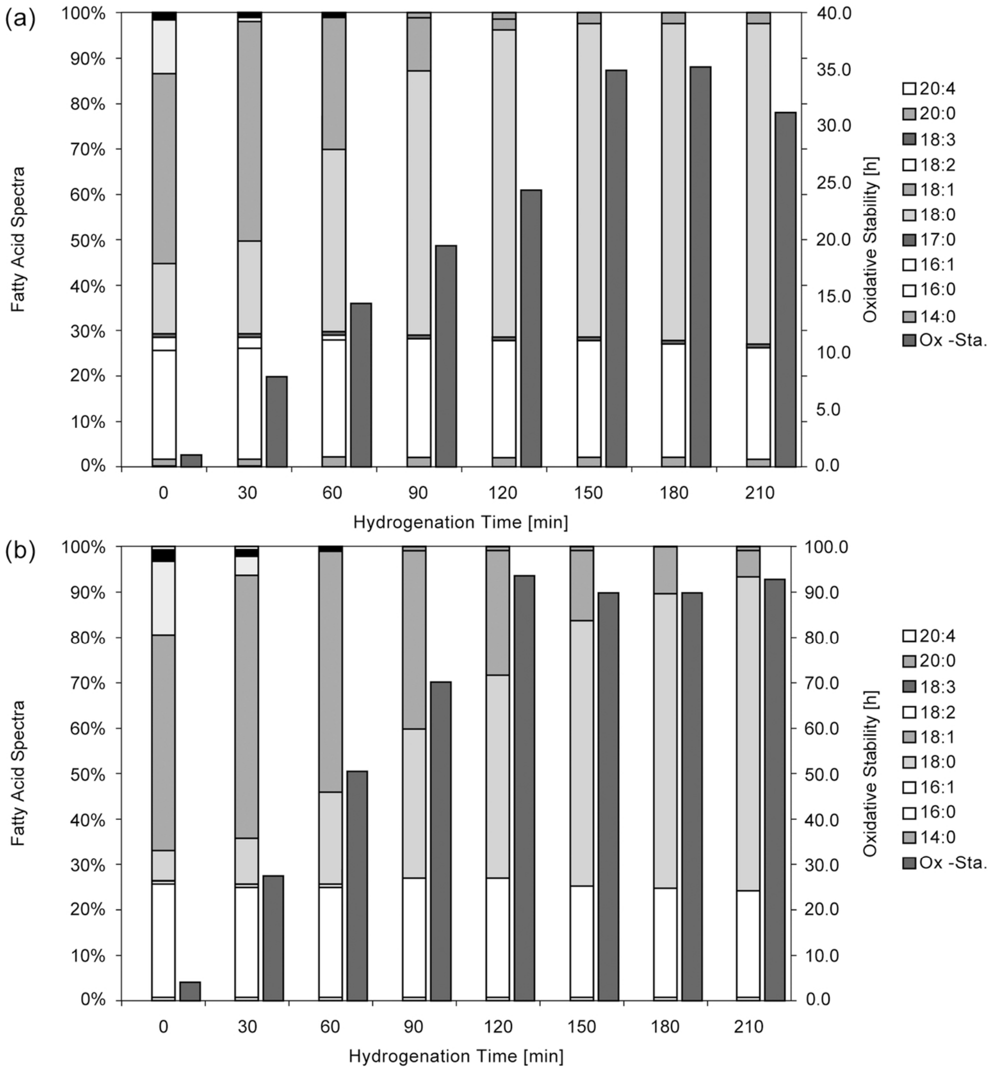
The mechanism involving the major surface species on the RuSnB/Al2O3 catalyst. Adapted with permission from ref. [106].
40x9mm (300 x 300 DPI)



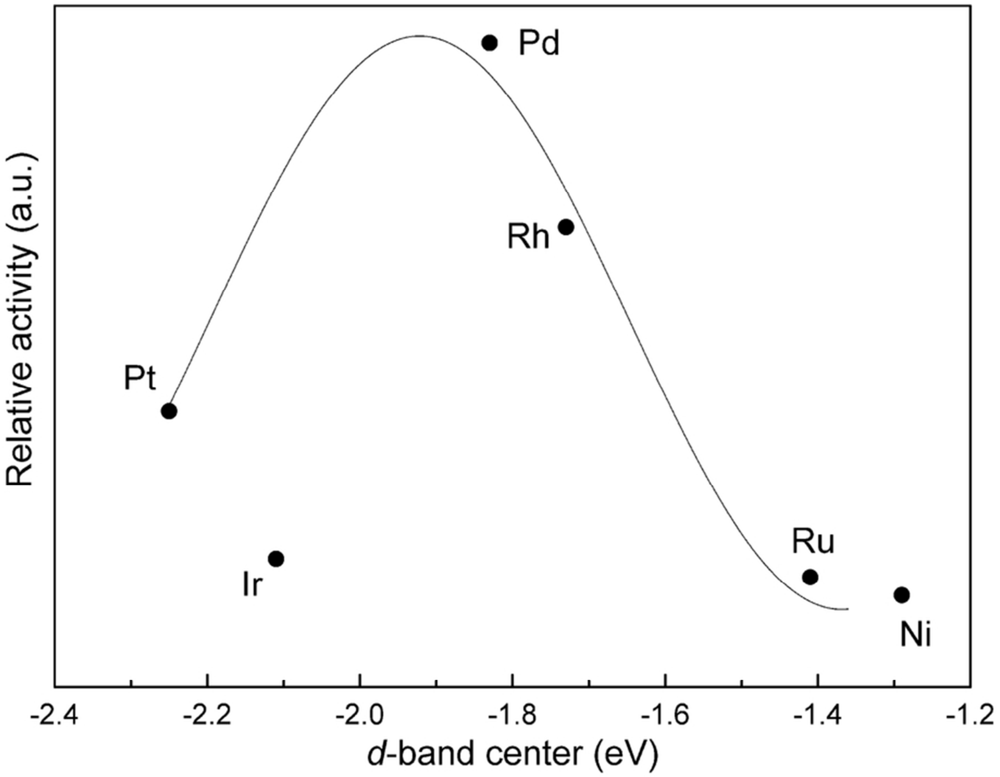
Mechanism of the direct hydrogenation of methyl oleate into unsaturated alcohol RuSn/Al2O3 catalyst.
Adapted with permission from ref. [118].
42x7mm (300 x 300 DPI)



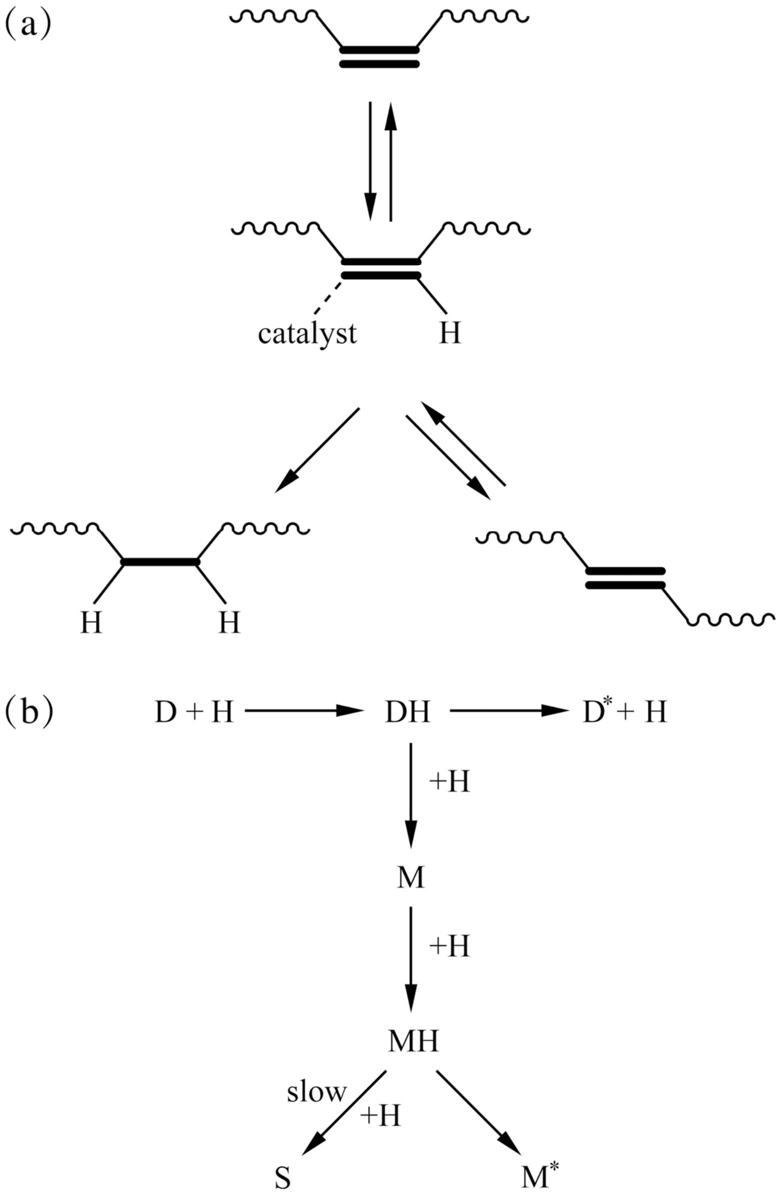
Possible chemical reactions involving hydrogenation of C=C and C=O in unsaturated FAMEs excluding isomerization, hydrodeoxygenation, decarbonylation, decarboxlation, and thermal decomposition.
105x79mm (300 x 300 DPI)



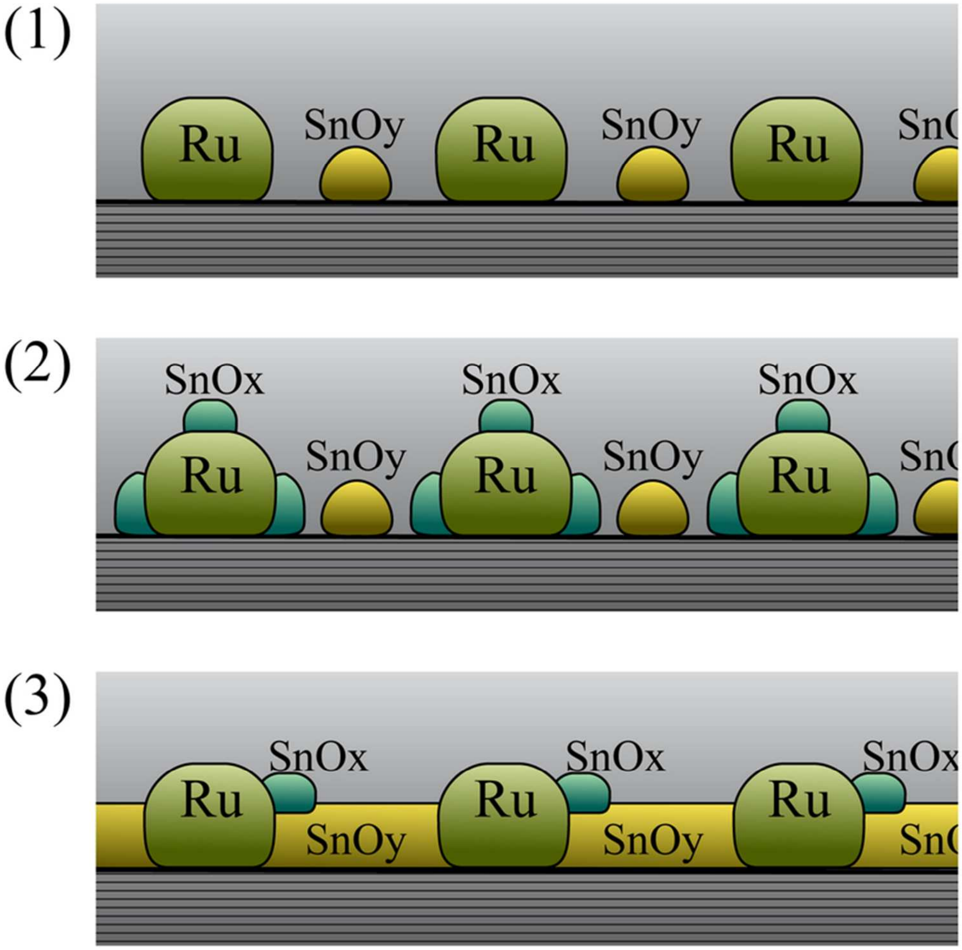
Fatty acid composition and oxidative stabilities of FAMEs hydrogenated from (a) fat from rendering plants and (b) used cooking oil. Reproduced with permission from ref. [20].
128x137mm (300 x 300 DPI)



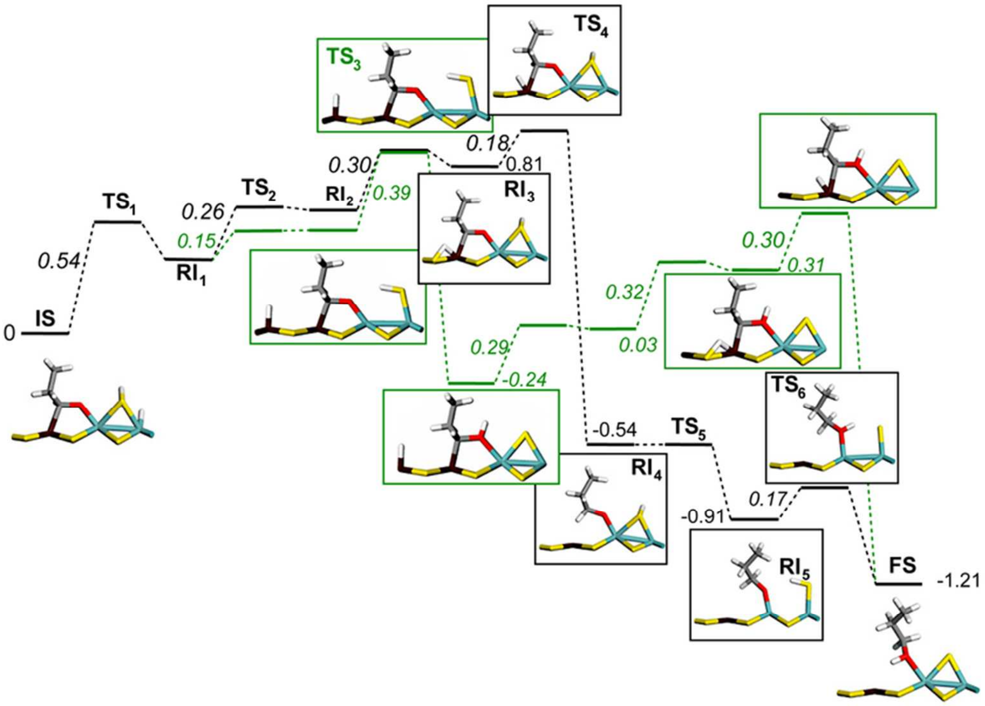
Correlation between the activity order and the d-band center of the metal towards hydrogenation of natural oils.
77x60mm (300 x 300 DPI)



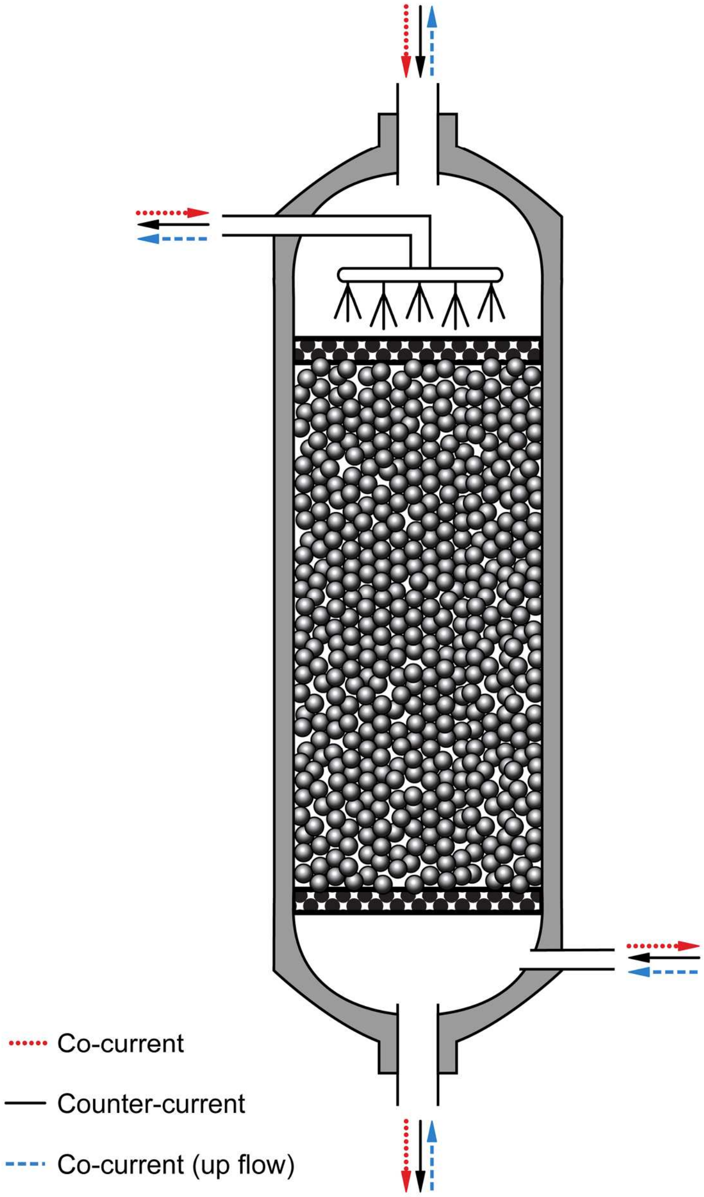
Reaction pathways of hydrogenation of C=C in (a) monounsaturated and (b) diunsaturated fatty acid. D, M, S and * represent diene, monoene, saturate and potentially isomerized, respectively. Adapted with permission from ref. [87].
119x178mm (300 x 300 DPI)



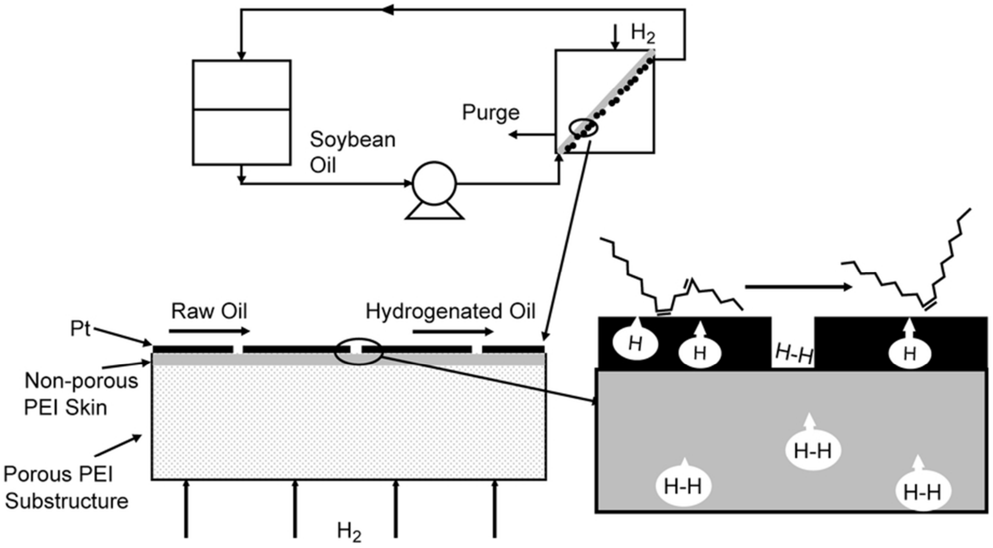
Model representating the RuSn centers with different tin contents: (1) Sn/Ru<4; (2) 4<Sn/Ru<5.5; (3) Sn/Ru>5.5. Adapted with permission from ref. [118].
71x72mm (300 x 300 DPI)



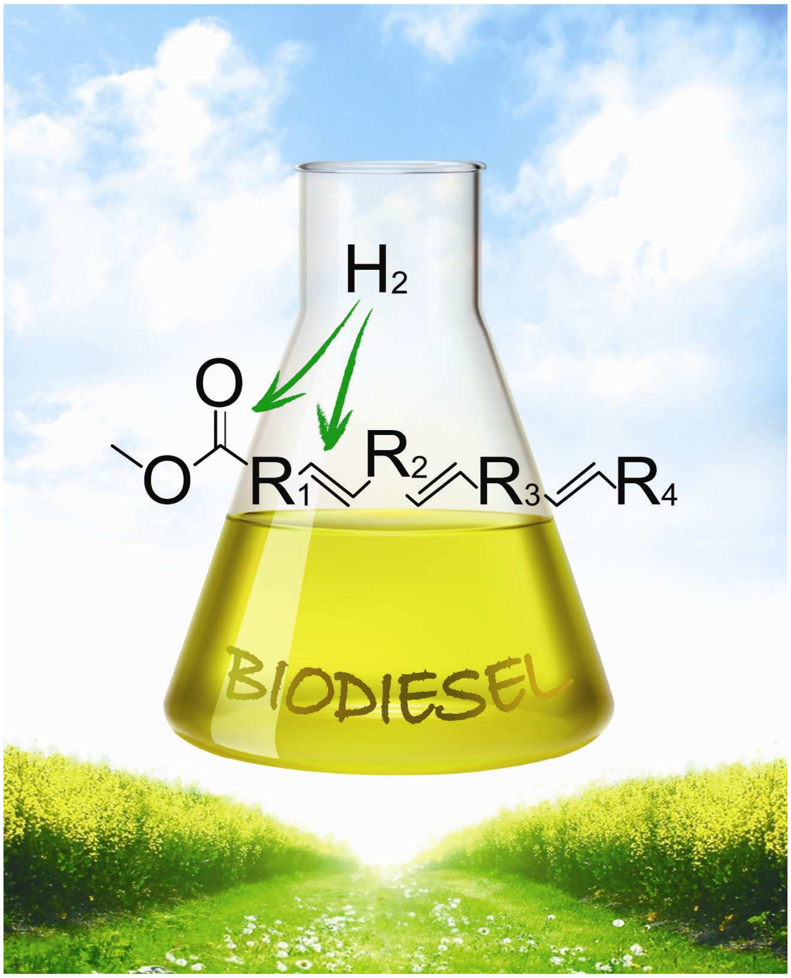
The two possible hydrogenation pathways of propanal on NiMoS: the propoxy route with first CH and then OH formation (black); the hydroxylpropl with first OH and then CH (green). The most stable coadsorption state between propanal and two hydrogen atoms is taken as reference. Energies are reported in eV. Reproduced with permission from ref. [134].
72x52mm (300 x 300 DPI)



Operating modes of fixed-bed multiphase catalytic reactors.
135x228mm (300 x 300 DPI)



Schematic of vegetable oil hydrogenation as it would take place in the catalytic membrane reactor. PEI represents the poly-ether-imide. Reproduced with permission from ref. [158].
78x43mm (300 x 300 DPI)



Review summarizing recent developments in hydrogenation of C=C and C=O in FAMEs focusing on catalysts, reaction mechanisms, and reactor conditions