

EFFECT OF CATALYST PROPERTIES ON THE DEOXYGENATION REACTION OF VEGETABLE OIL AND MODEL COMPOUND TO PRODUCE DIESEL RANGE HYDROCARBON FUELS: A REVIEW

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Abstract

The concern associated with the depletion of fossil fuel energy has opened up windows of opportunity for researchers to develop potential energy from renewable resources. The renewable green diesel with diesel range hydrocarbon structure has gained increasing popularity by removing oxygen molecule via direct or hydrodeoxygenation (HDO) and indirect or deoxygenation (DO) reaction. The catalyst design is an important key to achieve the high quality of diesel range hydrocarbon fuels. The different catalyst properties effect to the distribution of deoxygenated liquid product, the catalytic activity and coke formation during the reaction process. The interaction between metal and support catalyst causes electron transfer to give the synergetic effect. The acidity and basicity play important role in C-C and C-O breaking bond in triglyceride and prevent the coke formation. The pore structure and pore size catalyst provide the accessibility of active sites alleviates the diffusion limitation of reactants/ products.

Keywords: hydrocarbon fuels, green diesel, catalyst, properties

Introduction

The deficiency of fossil fuel, increasing of the energy demand and the environmental issue have been attracted the global attention for developing the renewable energy. Plant biomass are generally used in many studies as a feedstock to produce renewable biofuels. Lately, the first generation biofuels known as biodiesel have been developed (Kamaruzaman *et al.*, 2020). Biodiesel mainly consist of fatty acid methyl esters (FAME) that formed by vegetable oil transesterification (Choo *et al.*, 2020). Regrettably, the high oxygen contents in FAME lead the biodiesel produced vulnerable to oxidation, lower its heat content and heating value (HV) (Alsultan *et al.*, 2017; Hu *et al.*, 2019; Pattanaik and

Misra, 2017). Moreover, biodiesel exhibited poor cold-flow properties which can cause serious problems in conventional engine. Recently, green diesel with diesel range hydrocarbon structure have been expanded to overcome the detriment of biodiesel. The renewable green diesel was obtained by removing oxygen molecule via direct or hydrodeoxygenation (HDO) and indirect or deoxygenation (DO) reaction. However, HDO reaction consumed a large amount of H₂ which is not economically for industrial process. Alternatively, deoxygenation reaction can be regarded as very attractive with simultaneous advantage of no additional H₂ consumption during the process.



In deoxygenation reaction, green diesel is produced mainly via decarboxylation/-decarbonylation (deCO_x) reactions under H₂ or inert (H₂-free) atmosphere. Afterwards, oxygenates were removed from all fatty acid intermediates (C₁₆ and C₁₈) present in the vegetable oil or model compound to form CO₂, CO and H₂O as by product. Consequently, saturated and unsaturated hydrocarbon were produced with the carbon number reduced by one (C₁₅ and C₁₇) from the parent fatty acid (Silva *et al.*, 2018).

Catalyst design is an important key to achieve the high quality of diesel range hydrocarbon fuels. The catalyst for deoxygenation reaction should be active and selective to the formation of diesel range-hydrocarbon fractions. Undoubtedly catalyst support is crucial for enhancing the deoxygenation activity and product selectivity. Several catalyst support have been explored in deoxygenation reaction including activated carbon (Safa Gamal *et al.*, 2019), multi walled carbon nanotube (MWCNT) (Popov and Kumar, 2015), mesoporous SiO₂ (Zheng *et al.*, 2019), mesoporous TiO₂ (Oi *et al.*, 2020; Hengsawad *et al.*, 2018), ZrO₂ (Miao *et al.*, 2016), CaO (N. Asikin-Mijan *et al.*, 2017), Al₂O₃ (Loe *et al.*, 2016), Al-MCM-41 (Zhao *et al.*, 2017), SBA-15 (Baharudin, Taufiq-Yap, *et al.*, 2019), ZIF-67 (Yang and Carreon, 2017) and zeolites (Sousa *et al.*, 2018; Choo *et al.*, 2020). Among these, aluminosilicates-based support such as zeolites and mesoporous alumina/silica were the most promising candidates in deoxygenation reaction because of their porosity-acidity interplay (Gómez *et al.*, 2018; Xing *et al.*, 2018a; Zulkepli *et al.*, 2018). The porosity and surface area plays important role in reactant and product diffusion in active sites catalyst. Puértolas *et al.* also observed an outstanding decarbonylation reaction over hierarchical ZSM-5 zeolites

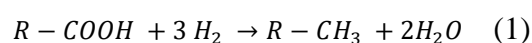
(Puértolas *et al.*, 2016) and suggested due to interplay between large Brønsted acid sites at the mesopore surface (Veses *et al.*, 2016). Noted, the acid properties also gives the important part in the formation of diesel range hydrocarbon fuels. Meanwhile, as reported by Gosselink *et al.*, (2013) basicity in catalyst played an crucial role in repressing the formation of coke along with promotion towards C-O cleavage through decarboxylation reaction. Concurrently, acidity is required to stimulate the C-C breaking during DO reaction (Hermida *et al.*, 2015).

Deoxygenation Reaction

Deoxygenation reaction is one of the alternative diesel range hydrocarbon fuels (green diesel) by oxygen removal from carboxylic group in fatty acid using solid catalyst (Hermida *et al.*, 2015). Deoxygenation reaction of fatty acid with hydrogen occur via direct (H₂ atmosphere, hydrodeoxygenation reaction) and indirect route (inert atmosphere). The hydrodeoxygenation reaction (HDO) will produce paraffin hydrocarbon and H₂O. The reaction pathway of fatty acid deoxygenation reaction includes liquid and gas phase reaction (Figure 1). In liquid phase, the hydrodeoxygenation (HDO), decarbonylation (DCO) decarboxylation (DCO₂), and de/-hydrogenation reaction occurs. In gas phase, the methanation and water gas shift reaction will produce CH₄, H₂, CO₂ gas and H₂O.

1. Hydrodeoxygenation reaction (HDO)

The HDO reaction involves the interaction between the reactant, catalyst and hydrogen during the reaction process at high temperature and pressure (Pattanaik and Misra, 2017).



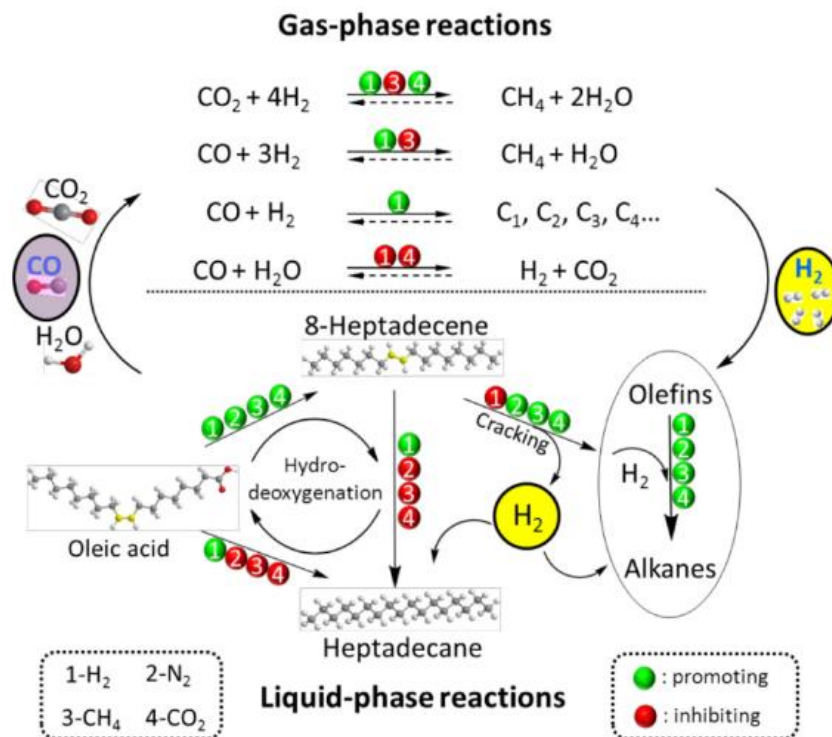
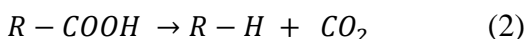


Figure 1. Proposed deoxygenation reaction under H₂ and inert atmosphere (Xing *et al.*, 2018)

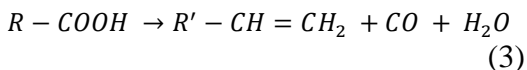
2. Decarboxylation reaction (DCO₂)

Decarboxylation reaction is the typical deoxygenation process that removes oxygen in the form of CO₂ and produce saturated hydrocarbon through direct C–C bond cleavage under mild conditions (Ooi *et al.*, 2019).



3. Decarbonylation reaction (DCO)

The decarbonylation reaction release oxygen from carboxyl groups by remove carbon monoxide and water molecules to produce alkenes/unsaturated hydrocarbon (Hermida *et al.*, 2015).

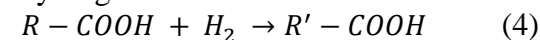


4. Dehydrogenation and hydrogenation reaction

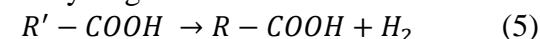
Hydrogenation reactions involve the breaking bonds in the unsaturated carbon chains of fatty acids in the presence of hydrogen (Hermida *et al.*, 2015). In contrary, the dehydrogenation reaction

release H₂ gas due to a cracking reaction or the formation of unsaturated hydrocarbons.

Hydrogenation



Dehydrogenation

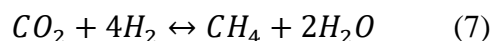
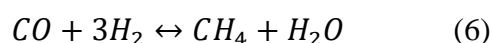


R= unsaturated hydrocarbon

R'= saturated hydrocarbon

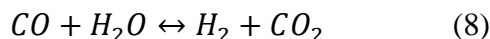
5. Methanation reaction

The methanation reaction is a reaction to the formation of methane gas. The CO and CO₂ gases produced in the deoxygenation reaction can react with H₂ to produces methane gas. This reaction is reversible.



6. Water Gas Shift (WGS) reaction

The The WGS reaction involve the reaction between CO gas and water to produce H₂ and CO₂ gases. This reaction is reversible.



Catalyst Design

The development of highly active, selective and stable catalyst with high reusability are some important requirements of catalyst that can be used for deoxygenation reaction of vegetable oil. Previously, the researchers used the simple molecule of fatty acid or triglyceride to represent the compound contained in vegetable oil. The fatty acid and triglyceride that used in deoxygenation reaction called as model compound. The use of model compound in deoxygenation reactions will make it easier for researchers to examine the mechanism of the reaction that occurs.

The catalyst design plays an important factor that needs to be considered before being applied in a chemical reaction. In the deoxygenation reaction, the pore size, surface area, the number of acidic/basic sites and the presence of alkaline metals are important factors which influence the catalytic activity of long-straight chain hydrocarbon fuels. Nowadays, various types and modifications of catalysts have been developed to increase the catalytic activity and selectivity in deoxygenation reactions.

The catalyst used in deoxygenation reaction can be classified to 3 group: metal/metal oxide, support and metal/metal oxide-support. Modification of metal to form bimetallic catalyst and metal/metal oxide-support catalyst also has been studied to enhance the performance of catalytic activity deoxygenation reaction (Loe *et al.*, 2016; Miao *et al.*, 2016). Metal/metal oxide that already used in deoxygenation reaction are Cu, W, Co, Ni, Li, Cs, Sn, Mg, Co-Ni,

Ni-Cu, Co-Ca, Pt, NiMo, Fe₂O₃, WO₃, PdSn, ZnO, ZrO₂, CaO, NiO and La₂O₃. Meanwhile, for the support that already used for deoxygenation catalyst are porous material such as SiO₂, ITQ-2, MCM-2, Al₂O₃, AC, MWCNT, SiO₂-Al₂O₃, MCM-41, SAPO-11 and SBA-15, zeolit beta, ZSM-5, USY, LSX, NaX and MOFs (Kubic'ka and Kubic'kova', 2010; Qian *et al.*, 2014; Xing *et al.*, 2018).

Catalyst Properties in Deoxygenation Reaction

The choice of catalyst plays an important role in the deoxygenation reaction in order to obtain high conversion and high selectivity in the formation of long chain hydrocarbons fuels. The interaction of metals with the catalyst support, acid strength, basicity of the catalyst, porosity, particle size and surface area are some of the catalyst properties that can affect catalytic activity in deoxygenation reactions (Table 1).

Interaction of metal and catalyst support

The interaction between the metal and the support catalyst can be analyzed using Temperature Programmed Reduction (H₂-TPR) instrument. Catalysts with different supports will show different TPR profiles which indicate the different interaction between the metal and the support catalyst. Kubička *et al.*, (2014) have studied using three different support catalysts of TiO₂, SiO₂ and Al₂O₃ with impregnated NiMo metal. The interaction between metal and the support catalyst will affect the size of the metal. The TPR profile of NiMo/TiO₂ shows a lower reduction temperature compared with SiO₂ and Al₂O₃ which indicates the weak metal interaction with the catalyst support. The weak interaction between metal and support catalyst will reduce the catalytic activity in deoxygenation reaction and decrease the selectivity of n-C₁₇₊₁₈ hydrocarbon.

Table 1. Reported studies with different catalyst properties in deoxygenation reaction of various vegetable oil and model compound

Catalyst	Reaction	Feedstock	Catalyst Properties					Selectivity (%)		Reference	
			Surface area (m ² /g)	Pore size (nm)	Pore volume (cc/g)	Acid sites (μmol/g)	Basic sites (μmol/g)	Conversion (%)	Hydro carbon		Carbon range
Al-MCM-41			739	3.8	0.85	185	-	51.8	51	31	(Nugraha, Prasetyoko, Bahruji, et al., 2021)
Ni/Al-MCM-41	DO-deCOx	RTO	372	3.55	0.52	796	-	68.3	72	62	C ₁₁₋₁₈
NiO-5CaO/SiO ₂ -Al ₂ O ₃			163.51	7.97	0.42	3005.7	533.4	-	85	48	nC ₁₅ +nC ₁₇
NiO-10CaO/SiO ₂ -Al ₂ O ₃	DO-deCOx	Triolein	127.64	10.54	0.38	1105	924.4	-	84	32	C ₁₇
Fe-CaO			7.37	2.87-188.6	-	32.13	523.74	-	44	38	
Zn-CaO			7.58	2.96-152.3	-	174.14	624.57	-	51	28	
Co-CaO	DO-deCOx	Triolein	7.88	2.9-116.5	-	257	568.56	-	55	43	C ₁₅ -C ₁₇
20%Ni-5%Cu/Al ₂ O ₃			129	8.8	0.28	-	-	98	>99	49	
Al-MCM-41			535.96	1.52		570	-	-	91	17	C ₁₇ C ₁₅
H-Al-MCM-41	DO-deCOx	Stearic acid	521.94	1.52	1.35	6260	-	-	96	27	C ₁₇ C ₁₅
S-ZSM-5			439	3.6, 5.6	0.47	158	-	6.73	45.94	63	
Al-MCM-41	DO-deCOx	JCO	739	3.8	0.83	296	-	20.04	83.68	92	C ₁₁₋₁₈
5%Pd/C			1042	2.6	0.65	-	-	58	95	87	
10%Ni/C	DO-deCOx	Stearic acid	374	3.8	0.3	-	-	19	50	26	C ₁₅₋₁₇

The synergy between the support catalyst and the active site can also cause a synergistic effect. This synergistic effect causes the transfer of electrons from Ni to Mo on the surface synergetic oxygen vacancy (SSOV) which can prevent the formation of coke on catalyst surface (Hu *et al.*, 2019). Schematic representation of Ni and Mo species before and after reduction is shown in Figure 2. Figure 2 (a1 and a2) describes the formation of surface vacancy oxygen (SVO) from Mo-□-Mo after the catalyst reduction step.

Figure 2 (b1 and b2) shows the formation of Ni attached to the catalyst surface after reduction of the Ni/A precursor using H₂. Figure 2 (c1 and c2) shows that bimetallic catalysts such as NiMo-A will form Ni-O-Mo species which will produce surface synergy oxygen vacancy (SSOV) of Ni-□-Mo after the reduction process. The synergistic effect between bimetallic catalysts and support could contribute new insight to the construct of new catalysts to improve better catalytic performance in deoxygenation reaction.

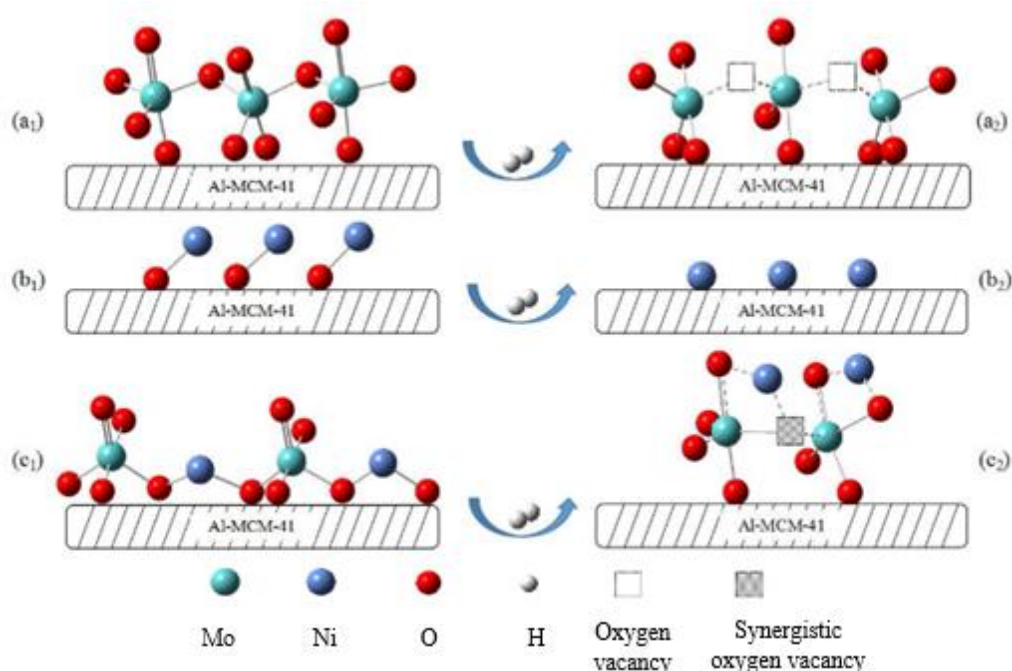


Figure 2. Schematic representation of Mo and Ni species on the surface of (a1) Mo/A precursor, (a2) Mo/A catalyst, (b1) Ni/A precursor, (b2) Ni/A catalyst, (c1) NiMo/A precursor, (c2) NiMo/A catalyst (Hu *et al.*, 2019)

Acidity of catalyst

The acidity of the catalyst acts as the active site of the catalyst which can break the C-C bond of triglyceride in the deoxygenation reaction. Catalyst with high acidity were noted to enhance C-O hydrogenolysis reaction and improve the selectivity of HDO products (Lup *et al.*, 2017). Catalyst support with large pore and surface area will provide place for metal impregnation. The good metal dispersion on catalyst surface will increase the number of acid active sites.

The research conducted by Kubička *et al.*, (2014) showed that the NiMo/SiO₂ catalyst had the highest number of acid sites compared to Al₂O₃ and TiO₂. Asikinmijan *et al.*, (2018) synthesized a bifunctional catalyst NiO-CaO/SiO₂-Al₂O₃ in the deoxygenation reaction of triolein. The results showed that among the weak, medium and strong acid sites, a catalyst with a medium-weak acid site was the most suitable for the decarboxylation-decarbonylation reaction. Strong acid sites will encourage cracking

reactions to produce molecules with short carbon chains hydrocarbon.

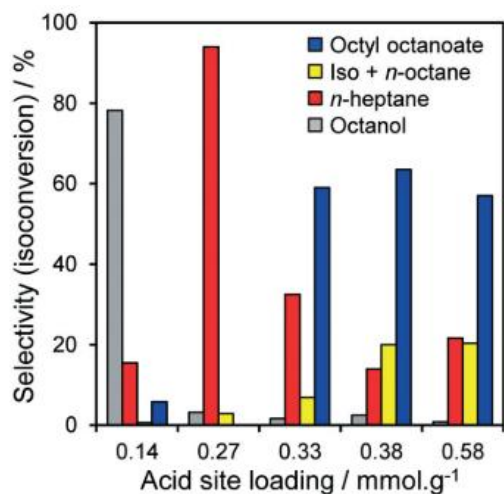


Figure 3. Product selectivity in octanoic acid hydrodeoxygenation over Ni/Al-catalysts as a function of acid site loading (Baharudin *et al.*, 2019)

Therefore, the Lewis acid is an important factor in deoxygenation reaction. The reducible oxide supports containing Lewis acid sites such as Cr₂O₃, ZrO₂, CeO₂ and TiO₂ are able to reduce the content of carboxylic acids to aldehyde (Rogers and Zheng, 2016). The Lewis acid sites have the capability to minimize carboxylic acids to aldehydes content and H₂O by oxygen chemisorption in carboxylic acid on catalyst surface by α -H abstraction. Meanwhile, the Bronsted acids was correspond to cracking capability and hydrogen transfer reactions (Wang *et al.*, 2019b). As reported in previous study by Baharudin, *et al.*, (2019) in Figure 3, Lewis acids are also observed to promote deoxygenation reaction via decarboxylation pathways to produce n-heptane. Furthermore, the increase of Brønsted acidity will increase the selectivity of octyl octanoate as by-product of esterification and is constant for samples with Si: Al < 75. Furthermore, as reported in our previous study, the increasing of Lewis acid sites by NiO impregnation enhance the catalytic

conversion of vegetable oil in to diesel-range hydrocarbon (Nugraha, *et al.*, 2021) and Brønsted acid correlated to cracking activity and hydrogen transfer reaction (Wang *et al.*, 2019).

Basicity of catalyst

As reported in previous studies, basicity characteristic is important to prevent the coke formation during the deoxygenation reaction process (Santillan-jimenez *et al.*, 2013). Asikin-mijan *et al.*, (2018) synthesized bi-functional catalyst NiO-CaO/SiO₂-Al₂O₃ for deoxygenation reaction of triolein. The results shows that basicity properties played an crucial role in repressing the formation of coke together with promotion against C-O cleavage via decarboxylation reaction (Gosselink *et al.*, 2013), meanwhile acidity is needed to provoke the C-C cleavage along DO reaction (Hermida *et al.*, 2015). In similar study reported the basicity and conversion increased in the order Fe-CaO < Ni-CaO < Co-CaO < Zn-CaO (N. Asikin-Mijan *et al.*, 2017). Incorporation of acid-base effect of Co-CaO and W-CaO were favour for the cracking and decarboxylation/-decarbonylation (deCOx) reactions to produce C₈₋₁₇ hydrocarbons as majority product.

Reangchim *et al.*, (2019) studied the mechanism of preventing coke formation on alkaline Sn catalyst. An illustration of the interaction of carbon atoms with the catalyst surface Ni and Sn is shown in Figure 4. On the surface of the Ni (111) catalyst, the value of $E_{ads} = -6.99$ indicates a strong chemisorption between carbon and Ni. Meanwhile, Ni₃Sn/Ni (111) showed lower E_{ads} . The bond distance between carbon atoms and 3 Ni atoms is 1.8 Å and the distance between Ni and Sn is 2.98 Å. This result shows that the chemisorption of carbon atoms is easier on Ni atoms than on Sn atoms or around Sn atoms. In Ni₂Sn/Ni (111), the chemisorption of carbon atoms is on the bridge between Ni₁ and Ni₂ atoms with

lower adsorption energy. These results indicate that the chemisorption of carbon is favored on the Ni atom and avoids the Sn (basic metal) atom or its surroundings. The interaction between carbon and the catalyst surface will decrease in the

presence of Sn metal. This result proves the catalytic study in deoxygenation reaction which basic metal will reduce the formation of coke and increase the deoxygenated liquid product.

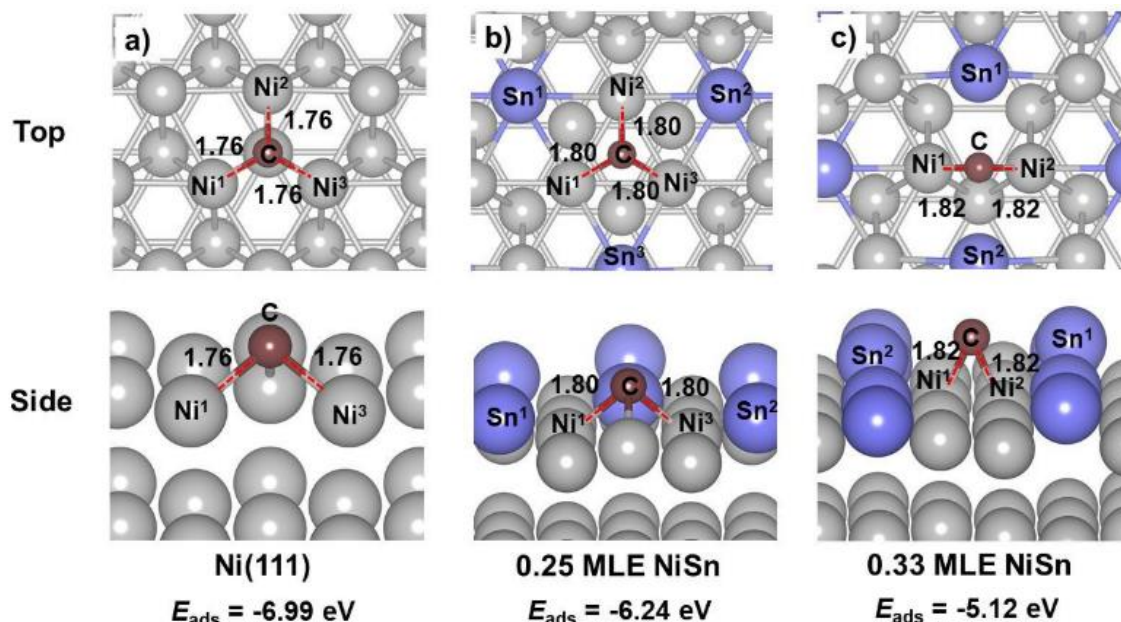


Figure 4. Top and side views of the most stable configurations of C atom on (a) Ni(111), (b) 0.25 MLE NiSn (Reangchim *et al.*, 2019)

Pore structure and pore size catalyst

The pore structure and pore size catalyst was investigated by Lee *et al.*, (2020) from SiO₂ microporous to mesoporous KIT-6, SBA-16 and SBA-15. The different structure of SBA-15 with two-dimensional p6mm symmetry hexagonal cylindrical pores, SBA-16 with cubic cage-like pores Im3m symmetry, and KIT-6 of gyroid cubic Ia3d with large-pores give influence in deoxygenation of methyl palmitate. The pore volume and pore size obtained were 1.00 cm³/g and 6.8 nm for SBA-15, 0.76 cm³/g and 3.9 nm for SBA-16, 0.98 cm³/g and 6.4 nm for KIT-6. Meanwhile for microporous SiO₂ gives 0.24 cm³/g for pore volume and very low intensity in mesopore pore size distribution. The

maximum yield of C₁₅₋₁₆ hydrocarbon of 73.5% with the minimum yield of palmitic acid of 3.7% was achieved by Ni impregnated on SBA-15. The increasing of catalytic activity can be contributed to the evidence that the mesoporous SBA-15 mitigate the diffusion restriction of reactants/products and enhance the active sites accessibility (Shi *et al.*, 2017). The diffusion restriction can be lessened in the order of cage-like structure SBA-16 > SBA-15 with parallel mesopore route > interconnected cubic structure from KIT-6.

The similar study was investigated by Oh *et al.*, (2022) by using Pt/Al₂O₃ with the pore size range of 3.3–28.6 nm. The effect of catalyst pore size was examined in deoxygenation of soybean oil.

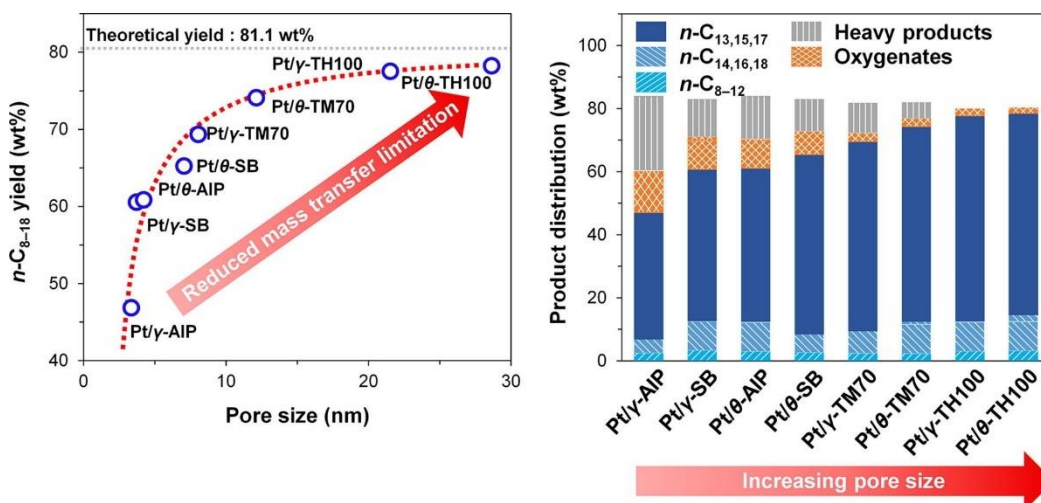


Figure 5. The liquid hydrocarbon yield distribution after 2 h reaction at 633 K in the function of pore size (Oh *et al.*, 2022)

As depicted in Figure 5, the pore size of catalyst affects to the liquid hydrocarbon distribution and formation of $n\text{C}_{8-18}$ hydrocarbon. The large mesopores (pore diameter $> \sim 12$ nm) were crucial to achieve maximum catalytic activity, reduce the mass transfer limitation and suppress catalyst deactivation. Catalyst Pt/ Al_2O_3 with extra-large mesopores of 28.6 nm in diameter gives the highest deoxygenation activity and selectivity to the formation of diesel range hydrocarbon. The higher pore size of catalyst also decreases the oxygenates species which declare the oxygen removal from carboxylic acid in triglyceride is the main route in deoxygenation reaction. Noteworthy to mention, the heavy products yield which are formed by the oligomerization of unsaturated fatty acid units also gradually decreased with increasing pore size.

Future Perspective

The production of diesel-range hydrocarbon fuels from vegetable oil and model compound highly relatable with catalyst properties. The catalyst properties discussed in this paper have their own role in catalytic deoxygenation reaction. The enhancement of conversion and selectivity towards diesel-range hydrocarbon influenced by the Lewis

acidity, high mesoporous surface area, and diameter. However, the use of acid-based catalyst may lead to the coke formation. Taking this into consideration, the use of bifunctional catalyst consist of acid-base active sites will be beneficial to produce high quality of diesel-range hydrocarbon fuels.

Conclusion

Deoxygenation of vegetable oils using supported metal catalyst to produce diesel-range hydrocarbon or green diesel are a promising alternative for advances renewable energy resources in the future. Hydrodeoxygenation, decarboxylation and decarbonylation are major reaction pathways for deoxygenation process. The key process to obtain highest catalytic activity in deoxygenation is the catalyst design. Small particle metal incorporated on mesoporous materials with medium-large pore and high surface area are recommended catalysts for vegetable oil or model compound deoxygenation to produce high yield or selectivity of diesel range hydrocarbons.

The catalyst design with desired properties is the important key to maximize the product yield in deoxygenation reaction. The interaction between the active site and the support catalyst can also cause a synergistic effect which improve better catalytic

performance in deoxygenation reaction. The acidity catalyst plays important role in breaking C-C bond in triglyceride and C-O hydrogenolysis reaction to enhance the selectivity of deoxygenated products. Meanwhile, basicity is important for inhibiting the coke formation during the deoxygenation reaction process. The pore structure and pore size catalyst provide the accessibility of active sites alleviates

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the diffusion limitation of reactants/products.

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