

**CHAPTER VII**  
**EFFECT OF SUPPORT ACIDIC PROPERTIES ON SULFUR TOLERANCE**  
**OF Pd CATALYSTS FOR PARTIAL HYDROGENATION**  
**OF RAPESEED OIL-DERIVED FAMES**

(Published in Journal of the American Oil Chemists' Society,

DOI 10.1007/s11746-012-2112-0)

### **7.1 Letter to the Editors**

The degree of saturation of fatty acid methyl esters (FAMES) has a strong effect on biodiesel fuel (BDF) properties especially oxidative stability and cold flow properties, i.e., the higher saturated FAMES component in biodiesel, the higher oxidative stability but the lower cold flow properties [1,2]. Therefore, partial hydrogenation of polyunsaturated FAMES is a promising solution to improve the oxidative stability.

Vegetable oil in the Cruciferae family such as rapeseed and canola oils are known to contain sulfur (S) compounds [3], which are powerful poisonous to the hydrogenation catalysts. However, the work carried out on S tolerance of the catalyst particularly for partial hydrogenation of polyunsaturated FAMES has not been done. Typically, using acidic supports is effective in increasing the S tolerance of noble metal [4]. Therefore, amorphous acidic materials have attracted considerable attention for using as supports for partial hydrogenation of vegetable oil. This work focused on the effect of support with different acidic properties: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, on S tolerance of Pd catalysts for partial hydrogenation of rapeseed BDF for improving its oxidative stability.

The partial hydrogenation was carried out in a batch-type reactor using Pd catalysts at the reaction conditions of 80°C, 0.3 MPa, 1000 rpm stirring rate and 200 ml/min H<sub>2</sub> flow rate. The Pd on acidic supports were prepared by the incipient wetness impregnation technique using Pd(NH<sub>3</sub>)<sub>4</sub>.Cl<sub>2</sub> with a total Pd loading of 1 wt.%. An exact amount of Pd(NH<sub>3</sub>)<sub>4</sub>.Cl<sub>2</sub> was dissolved in distilled water. Then, this solution was impregnated into the dried support and kept for 1 day. After that, the

catalyst was dried, calcined at 300°C for 3 h, and reduced at 300°C for 2 h before use in the partial hydrogenation reaction.

The specific surface areas and average pore diameters of the supports were measured by N<sub>2</sub> adsorption using a BELSORP 28SA. The surface area of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were 281.1, 248.9, and 384.5 m<sup>2</sup>/g, respectively, with an average pore diameter of 16.4, 12.1, and 8.1 nm, respectively. The acidity of the supports was measured by NH<sub>3</sub>-adsorption technique using an NH<sub>3</sub> calorimeter (CSA-450G).

After partial hydrogenation, a decrease in polyunsaturated FAMES with an increase of monounsaturated and saturated FAMES is clearly seen in Table 7.1. For the fuel properties, as expected, partial hydrogenation could improve the oxidative stability i.e., from 1.89 h of rapeseed BDF to 33.48 h after 1 h of hydrogenation using Pd/Al<sub>2</sub>O<sub>3</sub>. On the other hand, the pour point and cloud point of this hydrogenated BDF were observed to be worse as its increasing from -11°C to 12°C and from -3°C to 15°C, respectively. The activity of the catalyst was studied in terms of rate constants for each hydrogenation step, consequently from C18:3 to C18:2, C18:1, and C18:0, i.e.,  $k_1$ ,  $k_2$ , and  $k_3$ , respectively. These rate constants were determined based on the assumption of the first order irreversible reaction [6] using Polymath Professional 6.2. As presented in Table 7.2, the order of hydrogenation activity is: Pd/SiO<sub>2</sub> > Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > Pd/Al<sub>2</sub>O<sub>3</sub> despite the fact that Pd/Al<sub>2</sub>O<sub>3</sub> has the highest Pd dispersion ( $D_R$ ). This was due to the strong adsorption of the basic double bonds of unsaturated FAME molecules on the strong acidic sites of Al<sub>2</sub>O<sub>3</sub> support that retards their desorption and prevents the access of the other reactant molecules onto the surface of Pd particles. The adsorption of basic double bonds on the acidic support was also observed by Hu et al. [7]. They found that toluene, an electron-enriched aromatic compounds, strongly adsorb on the Al<sub>2</sub>O<sub>3</sub> support. In addition, Williams et al. [8] also suggested that the adsorption of tetralin occurs on two different sites, that is, on metal sites and on acid sites of the support.

**Table 7.1** FAME composition and some fuel properties of rapeseed BDF and hydrogenated BDF with and without additional S, after 1 h of reaction using Pd/Al<sub>2</sub>O<sub>3</sub> (in parenthesis is the composition of C18 FAMES)

	Rapeseed BDF	Hydrogenated BDF after 1 h (0.48 ppm S)	Hydrogenated BDF after 1 h (2.48 ppm S)
<b>FAMES composition (%)</b>			
Saturated FAME	7.14 (1.82)	23.79 (18.16)	12.17 (6.97)
Monounsaturated FAME	64.11 (62.42)	74.17 (72.68)	81.96 (80.25)
trans-Monounsaturated FAME	0.13 (0.10)	41.10 (40.18)	24.38 (23.88)
cis-Monounsaturated FAME	63.97 (62.32)	33.08 (32.50)	57.58 (56.37)
Diunsaturated FAME	19.55 (19.55)	0.86 (0.86)	4.44 (4.44)
Triunsaturated FAME	7.77 (7.77)	0.00 (0.00)	0.11 (0.11)
<b>Fuel properties</b>			
oxidative stability <sup>(a)</sup> (h)	1.89	33.48	13.21
pour point <sup>(b)</sup> (°C)	-11	12	2
cloud point <sup>(b)</sup> (°C)	-3	15	7

<sup>(a)</sup> Measured by Metrohm 743 Rancimat, according to EN 14112

<sup>(b)</sup> Measured by Tanaka mini pour/cloud point tester Series MCP-102, according to ASTM D6749

**Table 7.2** Acidic properties,  $D_R$ ,  $D_{RS}$ ,  $\theta$ , and rate constants of Pd on different supports

	Pd/SiO <sub>2</sub>	Pd/Al <sub>2</sub> O <sub>3</sub>	Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
Weak acid concentration <sup>(a)</sup> (mmol/g catalyst)	0.22	0.15	0.57
Medium acid concentration <sup>(a)</sup> (mmol/g catalyst)	0.00	0.08	0.25
Strong acid concentration <sup>(a)</sup> (mmol/g catalyst)	0.00	0.18	0.14
Total acid concentration (mmol/g catalyst)	0.22	0.41	0.96
Heat of adsorption of the strongest acid site (kJ/mol)	80.85	131.47	114.71
$D_R$ (%)	30.3	78.1	20.9
$D_{RS}$ (%)	0.66	2.06	1.31
$\theta$ (%)	97.8	97.4	93.7
$k_1$ ( $\times 10^2 \text{ min}^{-1} \cdot \text{mol surface metal}^{-1}$ )	115.21	34.84	84.93
$k_2$ ( $\times 10^2 \text{ min}^{-1} \cdot \text{mol surface metal}^{-1}$ )	97.64	28.00	53.79
$k_3$ ( $\times 10^2 \text{ min}^{-1} \cdot \text{mol surface metal}^{-1}$ )	5.86	2.57	4.61
$k_{1S}$ ( $\times 10^2 \text{ min}^{-1} \cdot \text{mol surface metal}^{-1}$ )	68.35	21.94	52.94
$k_{2S}$ ( $\times 10^2 \text{ min}^{-1} \cdot \text{mol surface metal}^{-1}$ )	43.94	14.38	32.56
$k_{3S}$ ( $\times 10^2 \text{ min}^{-1} \cdot \text{mol surface metal}^{-1}$ )	3.71	1.32	3.40
$k_{1S}/k_1$	0.59	0.63	0.67
$k_{2S}/k_2$	0.45	0.51	0.61
$k_{3S}/k_3$	0.63	0.51	0.74

<sup>(a)</sup> Acidic strength was classified by heat of adsorption: weak (70–90 kJ/mol), medium (90–110 kJ/mol), and strong (>110 kJ/mol) [5]

Furthermore, Pd dispersion after sulfidation in an H<sub>2</sub>S (500 ppm)/H<sub>2</sub> stream ( $D_{RS}$ ) was also determined and surface S coverage ( $\theta$ ) of Pd particles was calculated as follows [9]:  $\theta = (D_R - D_{RS})/D_R$ . Here,  $D_R$  and  $D_{RS}$  are Pd dispersion, after reduction and sulfidation, respectively, which were determined by pulse chemisorption of 10.1% CO/He [9,10]. The  $\theta$  indicates degree of poisoning by S, and S tolerance was in the following order: Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > Pd/Al<sub>2</sub>O<sub>3</sub> > Pd/SiO<sub>2</sub>. The higher S tolerance of Pd catalysts on acidic supports (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) was attributed to electron deficiency of Pd caused by acidic sites of the support, which contributed to the removal of electron from Pd [4,11]. Thus, S, which is an electron-withdrawing material, could not adsorb strongly on the Pd surface [11]. Therefore, the degree of S tolerance strongly depends on the amount of strong acidic sites.

In addition, the effect of support acidic properties on S tolerance was investigated through the hydrogenation of rapeseed BDF with the presence of 2 ppm of additional S at the same reaction conditions as that of original BDF (S content in original BDF = 0.48 ppm). Allyl isothiocyanate, which is naturally found in rapeseed oil [12], was used as a representative S compound. The FAMES hydrogenation activity before and after adding additional S was studied in term of the rate constants:  $k_1$ ,  $k_2$ , and  $k_3$ , and  $k_{1S}$ ,  $k_{2S}$ , and  $k_{3S}$ , respectively. After the addition of 2 ppm S, the activity decreased by about 30–50% of the original activity (Table 7.2), which exhibits lower amount of saturated FAMES in hydrogenated product (Table 7.1). The S tolerance of the catalyst was determined from the ratio of rate constants with and without additional S ( $k_{1S}/k_1$ ,  $k_{2S}/k_2$ , and  $k_{3S}/k_3$ ), which was in the following order: Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > Pd/Al<sub>2</sub>O<sub>3</sub> > Pd/SiO<sub>2</sub>. This order was consistent with the results obtained from H<sub>2</sub>S sulfidation experiments ( $D_{RS}$  and  $\theta$ ). Moreover, the same order of S tolerance in both experiments also revealed that the order of Pd-S affinity of each catalyst in both experiments was also the same. In  $D_{RS}$  measurements, Pd catalysts were sulfided at 280°C and the S tolerance was in a Pd-PdS<sub>x</sub> relationship [9]. On the other hand, in the FAMES hydrogenation experiment at 80°C, the Pd metal surface was not sulfided, only adsorbed by the S compounds via Pd-S interaction [9]. According to these results, use of an acidic support is a promising way to increase the S tolerance of Pd catalysts under low temperature conditions. Superiority in S

tolerance of acidic supports under high temperature conditions was already confirmed in our previous works [4,9].

However, Pd/Al<sub>2</sub>O<sub>3</sub> showed a higher S inhibitory effect than Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, despite possessed more strong acidic sites. This was due to steric hindrance from the strong adsorption between reactants and the Al<sub>2</sub>O<sub>3</sub> support that prevented the access of other reactant molecules to the Pd surface. The higher S inhibitory effect in  $k_{3S}/k_3$  of Pd/Al<sub>2</sub>O<sub>3</sub> over that of Pd/SiO<sub>2</sub> was also observed. The value of  $k_3$ , which shows a rate of reaction from C18:1 to C18:0 FAME, is the lowest, which means the most difficult reaction, so an accessibility of C18:1 FAME onto the Pd surface is quite important. This accessibility seems to be influenced more by steric hindrance via the adsorbed reactants over the Al<sub>2</sub>O<sub>3</sub> support [7,8]. Affinity of the reactants containing the basic double bonds to the acidic site is in the order of: 18:3 > 18:2 > 18:1 > 18:0

During hydrogenation, some of the original *cis*-monounsaturated FAMES were transformed into *trans*-configurations. The *cis*-monounsaturated FAME is preferable in terms of cold flow properties, since its melting point is lower than that of *trans*-isomers [13]. Therefore, it is significant to prepare a catalyst, which can reduce *trans*-isomerization selectivity. The selectivity towards *trans*-monounsaturated FAMES was in the following order: Pd/SiO<sub>2</sub> > Pd/Al<sub>2</sub>O<sub>3</sub> > Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (Table 7.3). The highest *trans*-monounsaturated FAME composition of Pd/SiO<sub>2</sub> was due to the weakest acidic strength of SiO<sub>2</sub>, causing a weak adsorption between basic unsaturated bonds of unsaturated FAMES and weak acidic sites of the support. After the unsaturated bond was hydrogenated by one H atom, part of the half-hydrogenated intermediate could rotate easily around its original double bond before the added H atom leaves, to form *trans*-isomers [14,15]. However, the *trans*-selectivity of Pd/Al<sub>2</sub>O<sub>3</sub> was observed to be higher than that of Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> even though it had more strong acidic sites. This could also be explained by the steric hindrance of strongly adsorbed reactants on Al<sub>2</sub>O<sub>3</sub>, which imposed a difficulty of other reactants and partially hydrogenated intermediate to access and adsorb on the active sites, and in turn led to weak adsorption and easy rotation of the partially hydrogenated intermediate, which finally generated *trans*-isomers. Yu et al. [16] also suggested that weak adsorption of tetralin on metal site causes the *trans*-decalin isomer to be preferred. Moreover, a higher S content in rapeseed BDF, lower

composition of *trans*-isomers was obtained. This was attributed to a decrease in metal sites, with the hindrance effect, after adding more S, resulting a greater difficulty in the rotation of the partial hydrogenated intermediate to generate *trans*-form. This result was in opposition to the hydrogenation of canola oil using Ni catalyst [17]. As for the Ni catalyst with loading amount of 25 wt.%, a larger surface of metallic sites still remained after the S inhibition, when compared with 1 wt.% Pd catalyst. However, the lower in electron density of Ni metallic sites after the S inhibition resulted in a lower affinity between the remaining Ni and the unsaturated compounds, which led to an easy in rotation of the partially hydrogenated intermediate and form the *trans* isomers. Therefore, using acidic supports and the addition of S is an efficient way to increase selectivity towards *cis*-isomers of Pd catalysts even though S acts as a poison to the catalyst, which affects the catalytic activity and stability.

**Table 7.3** Comparison of *trans*-monounsaturated FAMES composition at the same C18:2 and C18:3 conversion (~96%)

Conversion or FAMES composition (%)		Pd/SiO <sub>2</sub>	Pd/Al <sub>2</sub> O <sub>3</sub>	Pd/ SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
	C18:2 and C18:3 conversion	96.25	96.73	96.55
Without additional S	<i>cis</i> -monounsaturated FAME	34.62	33.08	36.68
	<i>trans</i> -monounsaturated FAME	43.36	41.10	38.21
	saturated FAMES	20.49	23.79	23.32
	C18:2 and C18:3 conversion	96.55	96.51	96.21
With additional S	<i>cis</i> -monounsaturated FAME	28.90	31.91	38.93
	<i>trans</i> -monounsaturated FAME	42.38	40.46	35.75
	saturated FAMES	26.52	25.59	23.33

According to these results, it can be concluded that the acidic properties of the support showed a significant effect on the S tolerance. The acidic supports (Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>) revealed a higher degree of S tolerance due to an electron deficiency of Pd metal caused by their acidic sites [10]. In addition, the

selectivity towards *cis*-isomers of the Pd catalysts could be increased by using acidic supports and the addition of S.

## 7.2 Acknowledgements

This work was financially supported by the Dutsadi Phipat Endowment Fund, Chulalongkorn University, Thailand. Special thanks to Dr. Takehisa Mochizuki, AIST, Japan, for his help with D<sub>RS</sub> analysis and Ms. Barbara Best for proofreading this manuscript.

## 7.3 References

1. Knothe G (2005) Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Process Technol* 86:1059–1070
2. Ramos MJ, Ferná'ndez CM, Casas A, Rodrí'guez L, Pe'rez A (2009) Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresour Technol* 100:261–268
3. Wijesundera RC, Ackman RG, Abraham V, deMan JM (1988) Determination of sulfur contents of vegetable and marine oils by ion chromatography and indirect ultraviolet photometry of their combustion products. *J Am Oil Chem Soc* 65:1526–1530
4. Yasuda H, Sato T, Yoshimura Y (1999) Influence of the acidity of USY zeolite on the sulfur tolerance of pd–pt catalysts for aromatic hydrogenation. *Catal Today* 50:63–71
5. Mochizuki T, Toba M, Morita Y, Yoshimura Y (2008) Effect of Yb loading on aromatic hydrogenation activity of Pd-Pt/USY zeolite catalysts. *J Jpn Pet Inst* 51:58–64
6. Naglic M, Smidovnik A, Koloini T (1998) Kinetics of catalytic transfer hydrogenation of some vegetable oils. *J Am Oil Chem Soc* 75:629–633
7. Hu S, Xue M, Chen H, Shen J (2010) The effect of surface acidic and basic properties on the hydrogenation of aromatic rings over the supported nickel catalysts. *Chem Eng J* 162:371–379



8. Williams MF, Fonfe B, Jentys A, Breitkopf C, van Veen JAR, Lercher JA (2010) Catalytically active sites of supported Pt catalysts for hydrogenation of tetralin in the presence of dibenzothiophene and quinoline. *J Phys Chem* 114:14532–14541
9. Yoshimura Y, Toba M, Matsui T, Harada M, Ichihashi Y, Bando KK, Yasuda H, Ishihara H, Morita Y, Kameoka T (2007) Active phases and sulfur tolerance of bimetallic Pd–Pt catalysts used for hydrotreatment. *Appl Catal* 322:152–171
10. Matsui T, Harada M, Bando KK, Toba M, Yoshimura Y (2005) EXAFS study on the sulfidation behavior of Pd, Pt and Pd–Pt catalysts supported on amorphous silica and high-silica USY zeolite. *Appl Catal* 290:73–80
11. Gallezot P, Bergeret G (1987) In: Petersen EE, Bell AT (eds) *Catalyst deactivation*. Marcel Dekker, New York, p 263
12. Kawakishi S, Kaneko T (1987) Interaction of proteins with allyl isothiocyanate. *J Agric Food Chem* 35:85–88
13. Knothe G, Dunn RO (2009) A comprehensive evaluation of the melting points of fatty acids and esters determined by differential scanning calorimetry. *J Am Oil Chem Soc* 86:843–856
14. Allen RR, Formo MW, Krishnamurthy RG, McDermott GN, Norris FA, Sonntag NOV (1982) In: Swern D (ed) *Bailey's industrial oil and fat products*, 4th edn. Wiley, Chichester, pp 1–95
15. Dijkstra AJ (2011) In: List GR, King JW (eds) *Hydrogenation of fats and oils: theory and practice*, 2nd edn. Am Oil Chem Soc Press, Champaign, pp 159–168
16. Yu Y, Fonfe B, Jentys A, Haller GL, Rob van Veen JA, Gutierrez OY, Lercher JA (2012) Bimetallic Pt–Pd/silica–alumina hydrotreating catalysts. Part II: structure–activity correlations in the hydrogenation of tetralin in the presence of dibenzothiophene and quinoline. *J Catal* <http://dx.doi.org/10.1016/j.jcat.2012.03.018>
17. deMan JM, Pogorzelska E, deMan L (1983) Effect of the presence of sulfur during the hydrogenation of canola oil. *J Am Oil Chem Soc* 60:558–562