

Short communication

Hydrogenation of soybean oil over various platinum catalysts: Effects of support materials on trans fatty acid levels

Hajime Iida^{*}, Daigo Itoh, Satoshi Minowa, Atsushi Yanagisawa, Akira Igarashi

Department of Applied Chemistry, Faculty of Engineering, Kogakuin University, 2665-1 Nakano-machi, Hachioji-shi, Tokyo 192-0015, Japan

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ABSTRACT

The effects of various support materials on the catalytic performance of supported platinum catalysts for the hydrogenation of soybean oil were examined. There was a linear relationship between the catalytic activity and the platinum dispersion of the platinum catalysts. Among the examined catalysts, Pt/BaSO₄ was effective for the reduction of both trans fatty acid (TFA) and additional saturated fatty acid (ASFA) levels in partially hydrogenated oils (iodine value (IV) = 70). In addition, the relationship between the TFA levels and the electronegativity of the metal ion in the support material was a volcano function.

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1. Introduction

The hydrogenation of vegetable oils is an important chemical process in the modification of fats and oils. The purpose of this process is to increase the melting characteristics and improve the oxidation stability of the liquid oils [1]. The process was patented in 1903 [2] and first commercialized by Procter & Gamble in 1911. As such, the use of margarine and vegetable shortenings rapidly increased as butter substitutes since the 1940s [3]. The hydrogenation processing of oils involves three reactions; the saturation of double bonds and both geometric (cis–trans) and positional isomerization. The chemical and physical properties of the hydrogenated oils are significantly influenced by the degree of unsaturation and the cis–trans isomerization of fatty acids. Trans fatty acids (TFAs), which are formed by geometric isomerization, have been associated with an increased risk of coronary heart disease (CHD) and several public health organizations have recommended that the intake of TFA be lowered as much as possible. This had led to a demand for reduced TFA formation during hydrogenation [4,5]. In the current hydrogenation technology for fats and oils, nickel catalysts are immersed in vegetable oils at temperatures of 393–473 K in the presence of hydrogen at approximately 0.1–0.5 MPa [6]. Lower temperatures and higher pressures result in lower TFA levels [7]; however, it has not been possible to produce partially hydrogenated oils with low TFA levels. There have been numerous studies for hydrogenation of vegetable oils over supported metal catalysts, with many reports on the various modifications of nickel, palladium, and platinum catalysts to reduce TFA levels during hydrogenation [8–18]. For example, Li

et al. reported that a nickel–boron alloy catalyst has a lower TFA selectivity for the hydrogenation of soybean oil [8]. Fernández et al. reported that the cis–isomer selectivity was improved by the molybdenum addition to Pd/Al₂O₃ prepared by sol–gel method [9]. McArdle et al. reported a platinum catalyst supported on mesoporous silica that had high catalytic activity and low TFA selectivity for the hydrogenation of sunflower oil [10]. In addition, they reported that the addition of nickel to Pt/SiO₂ catalyst improved the cis–isomer selectivity [11]. Hsu et al. have reported a Pd/Al₂O₃ catalyst with higher activity and lower TFA selectivity for the hydrogenation of canola oil than that for Pd/C and Pd/BaSO₄ catalysts [12]. The effects of the support material on the catalytic performance for the hydrogenation of vegetable oils over supported metal catalysts have long since been investigated; however there is still room for a systematic investigation of catalyst support materials.

The relationship between the TFA levels in partially hydrogenated oil and the electronegativity of metal ions in the support materials was systematically investigated for the hydrogenation of vegetable oils over platinum catalysts.

2. Experimental

2.1. Catalyst preparation

Supported platinum catalysts were prepared by a conventional impregnation method.

Al₂O₃, ZrO₂, CeO₂, TiO₂, MgO, and MoO₃ – x support materials were obtained by calcining JRC-ALO-6, JRC-ZRO-3, JRC-CEO-2, JRC-TIO-4, JRC-TIO-9, JRC-MGO-4 500A (reference catalysts of the Catalysis Society of Japan), and MoO₃ (Wako Pure Chemical Industries) at 673 K for 1 h in a stream of air, respectively. Colloidal silica (CARIAct Q-6, Fuji Silysia)

^{*} Corresponding author.

E-mail address: iida@cc.kogakuin.ac.jp (H. Iida).

Table 1
Catalytic properties and performance of various supported platinum catalysts.

Catalyst	BET surface area (m ² g ⁻¹)	Metal ion electronegativity in support material (–)	Platinum dispersion (%)	Catalyst concentration C _{Pt} × 10 ⁴ (g _{-Pt} g _{-oil} ⁻¹)	Reaction rate constant <i>k</i> (s ⁻¹ g _{-oil} g _{-Pt} ⁻¹)	TOF (s ⁻¹)
Pt/C	712	–	40.0	0.5	14.1	35
Pt/ZrO ₂	94	12.0	38.5	0.5	11.1	29
Pt/Al ₂ O ₃	177	11.3	31.6	0.5	9.3	30
Pt/SiO ₂ (Q-6)	268	17.1	23.0	0.5	9.0	39
Pt/SiO ₂ (MCM41)	839	17.1	29.9	0.5	7.5	25
Pt/SiO ₂ (SBA15)	644	17.1	36.8	0.5	12.3	33
Pt/TiO ₂ (TIO-4)	53	13.9	14.1	0.5	10.2	73
P/TiO ₂ (TIO-9)	91	13.9	43.8	0.5	11.8	27
Pt/CeO ₂	122	7.8	–	2.0	2.8	–
Pt/MgO	20	6.6	6.0	2.0	1.7	29
Pt/BaSO ₄	1	4.5	2.6	2.0	2.8	108
Pt/CaO	8	5.5	1.8	2.0	0.3	19
Pt/MoO _{3-x}	3	19.2	0.05	2.0	0.3	529

and mesoporous silica (SBA15 and MCM41) were used as SiO₂ supports. The MCM41 and SBA15 were prepared by a hydrothermal method [19]. A CaO support was obtained by calcining CaCO₃ (Wako Pure Chemical Industries) at 1173 K for 1 h in a stream of helium. BaSO₄ as a support was prepared by the precipitation method using BaCl₂ and Na₂SO₄ (Wako Pure Chemical Industries). Bis(acetylacetonato) platinum(II) (Tanaka Kikinzoku Kogyo) was used as the platinum precursor and platinum was loaded at 5 wt.%. A commercial nickel catalyst (SO-450, Sakai Chemical) for low TFA levels and a commercial Pt/C catalyst (STD, N. E. ChemCat) were used as reference catalysts.

2.2. Activity test

Hydrogenation of soybean oil (iodine value (*IV*) = 130) was performed using a small stainless steel batch reactor (25 cm³). Prior to the reaction, the catalysts were reduced at 673 K for 1 h. The reaction conditions employed were a catalyst concentration in the soybean oil of 50 or 200 ppm_{-Pt}, a reaction temperature of 413 K, and hydrogen pressure at 0.5 MPa. A stirring rate of 1700 rpm was employed because the apparent reaction rate was constant at the stirring rate above 1500 rpm. The composition of fatty acids in the hydrogenated oil was analyzed using flame ionization detector-gas chromatography (FID-

GC; capillary column, SP-2560, 100 m, 0.25 mm i.d.). Prior to the GC analysis, the triglycerides were converted into their fatty acid methyl esters (FAME) following the American Oil Chemists' Society (AOCS) official method [20]. The iodine value (*IV*) was estimated by the composition of fatty acids in the hydrogenated oil obtained by the GC analysis, where *IV* was defined as:

$$IV = M_{I_2} \sum Di(100 C_{w,i}/M_i) \quad (1)$$

where *M*_{I₂} (= 253.8 g mol⁻¹) is the molar mass of I₂, *Di* is the number of double bond in fatty acid *i*, and *C*_{w, *i*} is the mass concentration of fatty acid *i* (wt.%).

Assuming a first order rate equation with respect to *IV*, the reaction rate constant *k*, was calculated using:

$$-\ln(IV_t/IV_0) = kC_{Pt}t, \quad (2)$$

where *IV*₀ and *IV*_{*t*} are the iodine values at *t* = 0 and *t* = *t* (s), *k* (s⁻¹ g_{-oil} g_{-Pt}⁻¹) is the reaction rate constant, and *C*_{Pt} (g_{-Pt} g_{-oil}⁻¹) is the catalyst concentration based on platinum. Linear relationships between $-\ln(IV_t/IV_0)$ and *C*_{Pt}*t* were observed for all of the examined catalysts (data not shown).

2.3. Catalyst characterization

The Brunauer-Emmett-Teller (BET) surface area of the newly-prepared catalysts was determined by N₂ adsorption at 77 K using a flow absorption apparatus (Flow Sorb II 2300, Micromeritics). The composition of the flow gas was N₂:He = 30:70. The catalyst was degassed at 473 K for 15 min prior to the measurement.

The textural properties of Pt/SiO₂ catalysts were determined from nitrogen adsorption/desorption isotherm measurements at 77 K using a volumetric absorption apparatus (ASAP2010, Micromeritics). The pore size distribution was generated from a Barrett-Joyner-Halenda (BJH) analysis of the adsorption branches.

The amount of chemisorbed CO on the catalysts reduced at 673 K was estimated using a volumetric absorption apparatus (ASAP2010, Micromeritics) with a chemisorption unit. Adsorption isotherms for CO adsorbed on the catalysts were obtained at 308 K.

The platinum dispersion (*D*_{Pt}) of the catalysts was calculated from the amount of chemisorbed CO, where *D*_{Pt} was defined as:

$$D_{Pt} = \{V_{CO}f_{CO/Pt}/0.0224\}/\{L_{Pt}/M_{Pt}\}, \quad (3)$$

where *V*_{CO} (m³_{-STP} g_{-cat}⁻¹) is the amount of chemisorbed CO on the catalyst, *L*_{CO} (–) is the Pt content in the catalyst, *f*_{CO/Pt} (= 1.0) is the stoichiometric factor for CO chemisorption on Pt, and *M*_{Pt} (= 195.1 g mol⁻¹) is the molar mass of Pt.

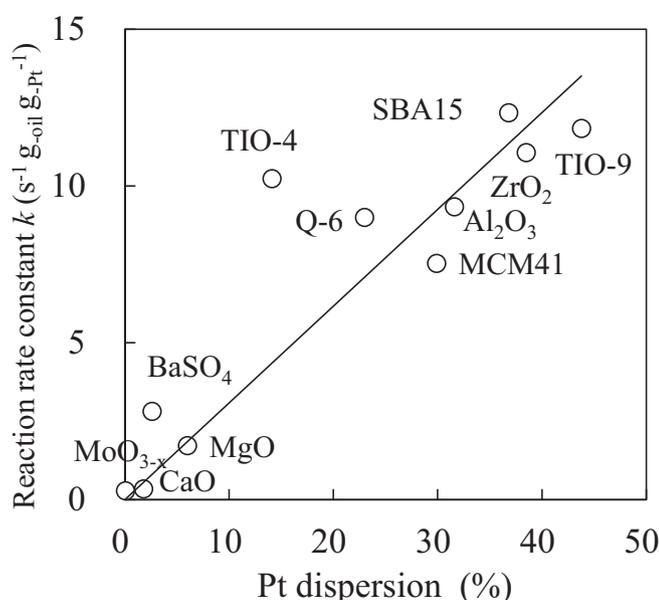


Fig. 1. Relationship between the catalytic activity and platinum dispersion of supported platinum catalysts.

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