

Short communication

Supported fluoro-perovskite catalysts for bio-diesel fuel production from waste and non-edible oils



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ABSTRACT

This work investigated the production of bio-diesel fuel from vegetable oils with free fatty acids (FFAs) using supported fluoro-perovskites (MCaF_3 ; M: K, Rb, Cs) as heterogeneous basic catalysts. The catalytic activities of supported $\text{M}\text{CaF}_3/\text{SiO}_2$ catalysts were found to decrease in the following order: $\text{Cs} > \text{Rb} > \text{K}$. In addition, these $\text{M}\text{CaF}_3/\text{SiO}_2$ catalysts showed greater tolerance to FFAs than a standard heterogeneous basic catalyst CaO .

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1. Introduction

Oils and fats have higher combustion heat than many other types of biomass, and most are liquids at ambient temperatures. Both of these characteristics are desirable for vehicle fuels. However the dynamic viscosities and flash points of oils and fats are overly high, so the triglycerides that are the main components of these materials must be converted to fatty acid methyl esters (FAMES) by transesterification to obtain alternative fuels meant to replace diesel oils, known as bio-diesel fuels (BDFs). The exhaust emissions of BDFs are relatively clean because they contain little sulfur oxide and produce minimal particulate matter. In addition, the combustion of BDFs maintains a carbon neutral system [1–4].

Homogenous basic catalysts such as KOH are currently used for the production of BDFs, so significant amounts of alkaline waste streams are generated during these production processes. Many researchers have studied heterogeneous basic catalysts for the transesterification of triglycerides as a means of mitigating this problem. A great number of solid basic catalysts have been reported in this regard, including alkali earth oxides [5–11] metal oxides [11–14], basic zeolites [15], hydrotalcite [16,17], and alkaline salts [9–10,16–24]. As an example, Veriziu et al. determined that alkaline fluoride catalysts supported on mesoporous alumina efficiently promote the transesterification of fatty esters with methanol. The order of the catalytic activities of these alkaline fluorides was found to be $\text{CsF} > \text{KF} > \text{LiF}$, and these activities were correlated with the basicity levels determined by carbon dioxide temperature-programmed desorption (CO_2 -TPD) [22]. For environmental reasons, it would be helpful to use waste edible oils as feedstocks for BDFs. In

addition, in order to avoid competition between BDFs and food supplies, non-edible vegetable oils are also desirable as feedstocks [3,9,11,14,25–27]. Although the presence of water and free fatty acids (FFAs) in waste and non-edible oils can lead to serious catalyst deactivation, Han et al. have reported that a KF/CaO catalyst exhibits high catalytic activity when used in conjunction with Chinese tallow seed oil, which contains FFAs, during the production of BDFs [18]. The same group also concluded that the formation of KCaF_3 is the main reason for this increased activity. However, potassium hydroxide is known to be generated along with KCaF_3 , as in the following equation,



Therefore, it may be that the potassium hydroxide contributes to the superior catalytic activity of KF/CaO .

The purpose of the present study was to explore the effects of both the support and the alkali metal on the catalytic performance of supported fluoro-perovskite (MCaF_3 , M: K, Rb, Cs) catalysts during the transesterification of fatty esters containing a FFA. This ester/FFA mixture served as a model waste non-edible oil.

2. Experimental

Supported fluoro-perovskite catalysts were prepared by a conventional impregnation method. SiO_2 , ZrO_2 , TiO_2 , and Al_2O_3 , acting as supports, were obtained by calcining CARIACT Q-3, 6, 10 (Fuji Silysia), JRC-ZRO-3, JRC-TIO-4, and JRC-ALO-6 (obtained as reference catalysts from the Catalysis Society of Japan), respectively, at 773 K for 1 h in a stream of air. Activated carbon (FY-1, Cataler) was also used as a support. A mixed solution containing an alkaline fluoride (MF, where M = K, Rb, Cs) together with calcium hydroxide (M: Ca = 3:1 on a

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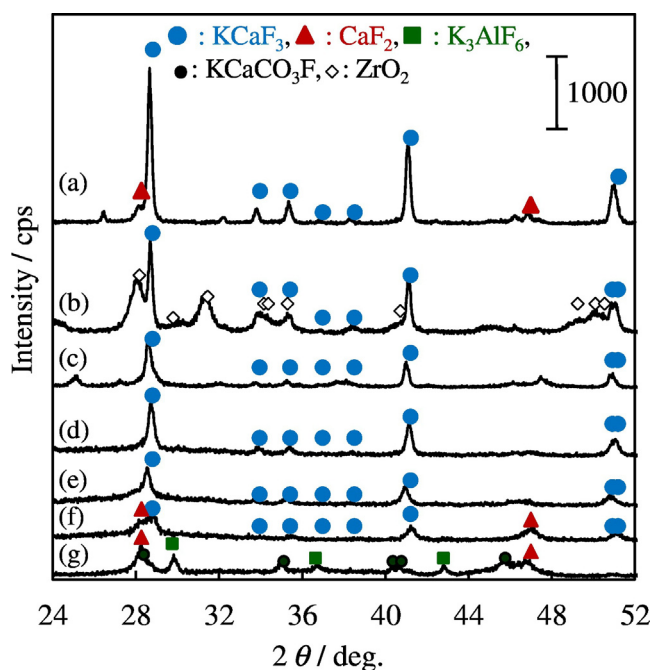


Fig. 1. XRD profiles of as-prepared KCaF₃ catalysts with various supports: (a) activated carbon, (b) ZrO₂, (c) TiO₂, (d) SiO₂ (Q-3), (e) SiO₂ (Q-6), (f) SiO₂ (Q-10), and (g) Al₂O₃.

molar basis) was combined with the support powder in a dish and the water was evaporated over a water bath at 373 K. The resulting material was further dried at 373 K for 12 h and then calcined at 773 K for 1 h in a steam of air. The desired fluoro-perovskites were formed during the calcination step according to the following equation,



In order to eliminate the potassium hydroxide byproduct from the catalyst, the material obtained from calcination was washed three times with methanol and then dried at 373 K for 12 h. The MCAf₃ was subsequently loaded onto the support at 5.7 mmol_{MCAf₃} g⁻¹_{support}. CaO was also produced as a reference catalyst by calcining calcium carbonate (Wako Pure Chemical Industries) at 1173 K for 2.5 h in a stream of helium [5].

The transesterifications of pure soybean oil and soybean oil combined with an FFA (as a model waste oil) were performed using a batch reactor with a volume of 25 cm³. The reaction conditions were as follows: amounts of oil and methanol: 4.6 g and 2.0 g,

Table 1
Physicochemical properties and catalytic performances of the supported MCAf₃ catalysts for the transesterification of soybean oil.

Alkali metal	Support	BET surface area ^a (m ² g ⁻¹)	MCAf ₃ crystallite size ^b (nm)	BDF yield ^c (%)
K	Activated carbon	960	43.4	4.7
	ZrO ₂	94	45.3	4.2
	TiO ₂	52	41.3	10.5
	Al ₂ O ₃	161	-	3.2
	SiO ₂ (Q-10)	248	23.0	11.3
	SiO ₂ (Q-6)	275	22.3	54.0
	SiO ₂ (Q-3)	306	22.3	67.5
Rb	SiO ₂ (Q-3)	306	22.3	67.5
Cs	SiO ₂ (Q-3)	306	23.0	71.4

^a Support.

^b (202).

^c FFA: 0 wt%.

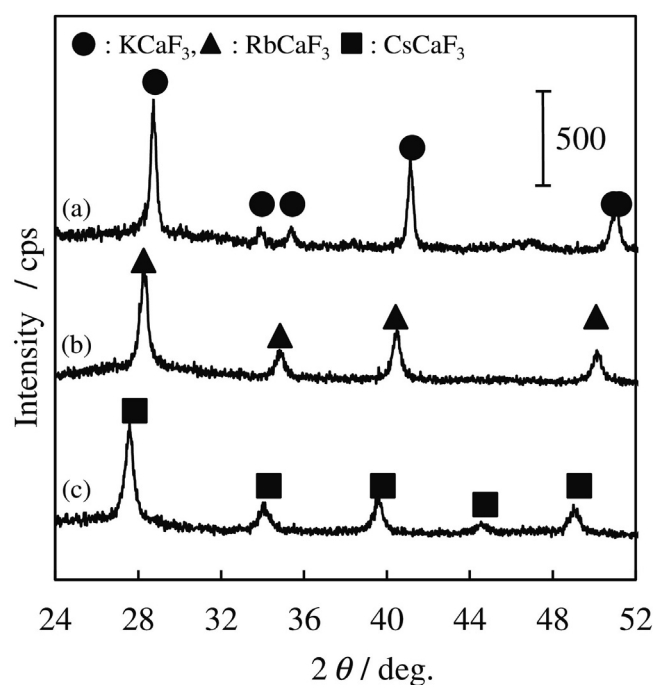


Fig. 2. XRD profiles of as-prepared MCAf₃ (M: K, Rb, Cs)/SiO₂ (Q-3) catalysts, where M is: (a) K, (b) Rb, and (c) Cs.

respectively (equivalent to a methanol to oil ratio of approximately 12 mol_{MeOH} mol_{oil}⁻¹), reaction temperature: 338 K, catalyst concentration: 21 mg_{cat.} g_{oil}⁻¹, FFA (oleic acid) concentration: 0 or 2 wt%, stirring rate: 850 ppm, reaction time: 30 min. The amounts of FAMES produced were determined using a flame ionization detector/gas chromatograph (FID-GC; SP-2560 capillary column, 100 m, 0.25 mm i.d.) in conjunction with oleic methyl ester as the internal standard.

The Brunauer–Emmett–Teller (BET) surface areas of the newly-prepared catalysts were 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 on a volume basis. Each catalyst was degassed at 473 K for 15 min, prior to measurement. X-ray diffraction (XRD; RINT2000, Rigaku) analysis was performed using Cu Kα

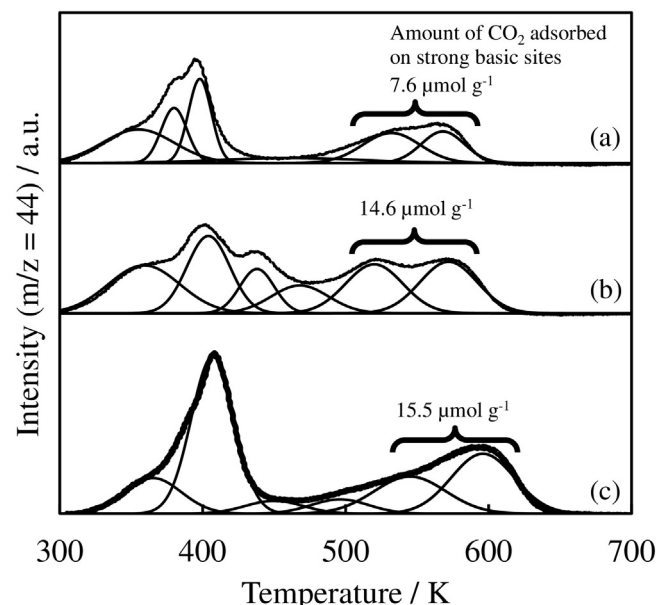


Fig. 3. CO₂-TPD profiles of MCAf₃/SiO₂ (Q-3) catalysts, where M is: (a) K, (b) Rb, and (c) Cs.

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