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Short communication

Preparation and characterization of fluorine modified oxides for transesterification

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ABSTRACT

KF supported Mg_3Al and $Mg_3Al_{0.6}La_{0.4}$ oxides were respectively synthesized by wet impregnation. The catalyst samples were characterized by BET, ICP-AES, XRD, XPS and CO_2-TPD. The results exhibited that the decomposition of KF modified hydrotalcites resulted in fluoride impregnated oxides. The basicity of KF supported oxides was improved due to the alkaline fluoride compounds. The catalysts were tested in the transesterification of waste cooking oil and methanol. A FAME yield (98.9%) was observed with a methanol to oil molar ratio of 12:1 and 3 wt.% catalyst amount in 8 h at 338 K.

1. Introduction

The biodiesel is an excellent alternate for fossil diesel because of its advantages such as free of sulfur, decreasing greenhouse emissions, renewable and environment friendly. The raw material of biodiesel could be vegetable oil, such as palm oil [1,2], sunflower oil [3,4], soybean oil [5–7], rap oil [8], as well as animal fat [9], or even waste cooking oil [10,11]. In order to economically produce biodiesel, unrefined inedible oil is used as raw oil for biodiesel production in recent years [12].

The solid base catalyzed transesterification is fast, less corrosive and easy to separate from product. Hydrotalcites (HTs) and hydrotalcite-like compounds are considered to be structure controllable layered double hydroxides materials, which have divalent and trivalent metal cations and intercalated anions [13]. The utilization of calcined hydrotalcites in the transesterification has been reported because of some interesting properties of hydrotalcites [14]. The transesterification of triglycerides for biodiesel production was investigated using MgAl hydrotalcite [15]. In order to improve catalytic properties, other hydrotalcite-like catalysts containing transition metal [16,17], rare earth metal [18] and KF [19] were reported. In this paper, KF supported solid base catalysts were synthesized to improve the basicity of catalysts. The basic sites were characterized by BET, ICP-AES, XRD, XPS and CO_2-TPD. The activity of solid base catalysts was tested in the transesterification of waste cooking oil and methanol.

2. Experimental

2.1. Catalyst preparation

The Mg_3Al_1 and $Mg_3Al_{0.6}La_{0.4}$ HTs samples were synthesized with 3 mole ratio of M^{2+} to M^{3+} (M for cation) by co-precipitation method at constant pH. The metal nitrates aqueous solution (A) containing $Mg(NO_3)_2{\bullet}6H_2O$ (38.46 g), $Al(NO_3)_3{\bullet}9H_2O$ (11.25 g) and $La(NO_3)_3{\bullet}6H_2O$ (8.66 g) and alkaline solution (B) including NaOH (11.02 g) and Na_2CO_3 (7.28 g) were slowly mixed together under constant stirring in a flask for 1 h. The pH of the mixture was maintained at 9.8–10.2 by controlling titration speed. The precipitate was left to age at 348 K overnight and subsequently washed with deionized water until the washings attained a pH of 7. The solid obtained was dried at 333 K in vacuum oven for 20 h. The resulting $Mg_3Al_{0.6}La_{0.4}$ HT was calcined at 773 K for 8 h to obtain oxide. The Mg_3Al_1 catalyst was prepared by the same process.

The potassium fluoride supported Mg_3Al_1 and $Mg_3Al_{0.6}La_{0.4}$ catalyst was prepared by wet impregnation. The prepared $Mg_3Al_{0.6}La_{0.4}$ oxide (5.00 g) and potassium fluoride solution containing $KF{\bullet}2H_2O$ (1.50 g) were mixed together under vigorously stirring. The $Mg_3Al_{0.6}La_{0.4}$ oxide was rehydrated in potassium fluoride solution at room temperature for 12 h. The decarbonated deionized water was used to prevent CO_2. The solution was dried at 333 K in vacuum oven for 20 h. The precipitate obtained was filtered, washed and calcined at 773 K for 8 h to

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obtain KF/$Mg_3Al_{0.6}La_{0.4}$ catalyst. KF/Mg_3Al_1 catalyst was prepared by the same process.

2.2. Characterization method of catalyst

The chemical composition of catalysts was determined by inductively coupled plasma atomic emission spectrometry (Varian 710ES). Surface area and pore size distribution were measured by BET method (Micromeritrics ASAP-2400) after degassing the samples at 77 K for 7 h. Solid catalyst morphologies and crystallite sizes were analyzed by powder X-ray diffraction (Rigaku D/max2550VB/PC) operating with CuKα radiation (λ = 1.5406 Å), at 100 mA, 45 kV, 2θ scanning range 10–80° and a step size of 0.02° (2θ). X-ray photoelectron spectroscopy was performed with AlKα radiation (Thermo Fisher ESCALAB 250Xi). The charging effect was corrected by the C_{1s} peak at 284.6 eV. The basicity of catalysts was analyzed by the temperature programmed desorption (TPD) with CO_2 (Micromeritics Autochem 2920). The samples were activated at 623 K for 1 h and then cooled to 313 K under helium flow. After that, the samples were saturated with dry CO_2 at the same temperature. Subsequently, the samples were purged with helium flow and the CO_2-TPD performer at a rate of 10 K/min to 1273 K.

2.3. Catalytic tests

A certain amount of raw oil (soybean oil or waste cooking oil), anhydrous methanol and catalysts were added to a glass reactor with condenser and magnetic stirring. After a certain reaction time, the products were filtered and stratified. The upper layer product was washed and extracted. The fatty acid methyl ester (FAME) in products was determined by gas chromatograph, equipped with phenyl-methyl-polysiloxane capillary column, flame ionization detector, according to EN 14103. A known amount of methyl heptadecanoate was added as internal standard. The analytical conditions for GC were as follows: injector temperature 523 K; column initial temperature 353 K; program rate 10 K/min; final temperature 473 K; detector temperature 523 K.

3. Results and discussion

3.1. Catalyst characterization

The textural properties of oxides are displayed in Table 1. ICP-AES analysis exhibited that the experimental value of metal composition of Mg_3Al_1, KF/Mg_3Al_1, $Mg_3Al_{0.6}La_{0.4}$ and KF/$Mg_3Al_{0.6}La_{0.4}$ catalysts were close to their theoretical value. The average pore size values were between 21.89 and 24.90 nm. The BET analysis showed that the deposition of KF on oxides surface decreased their surface area because of the decrease of micropore [20].

The XRD patterns of Mg_3Al_1, KF/Mg_3Al_1, $Mg_3Al_{0.6}La_{0.4}$ and KF/$Mg_3Al_{0.6}La_{0.4}$ catalysts are shown in Fig. 1. The diffraction peaks of Mg_3Al_1 oxide (a) were reflected at 36.9°, 42.9° and 62.3°. Those diffraction peaks were sharp and symmetrical, which corresponded to MgO crystallites. After KF species were impregnated on Mg_3Al_1 oxide, new crystallite $KMgF_3$ (31.7°, 39.1°, 45.4°, 56.5°, 66.2°) could be observed in XRD pattern of KF/Mg_3Al_1 oxide (b) in addition to MgO crystallites. Two main crystalline phases MgO and La_2O_3 (27.0°, 29.2°, 31.3°) could be observed in XRD pattern of $Mg_3Al_{0.6}La_{0.4}$ oxide (c). After the impregnation of KF, new diffraction peaks due to LaOF crystallites appeared at 26.9°, 31.0°, 44.8°, 52.8° in the XRD pattern of KF/$Mg_3Al_{0.6}La_{0.4}$ oxide (d).

Table 1
Chemical composition of catalysts and textural characterization of catalysts.

Sample	Mg/Al/La		BET Surface area(m^2/g)	Pore size(nm)
	Theoretical	Experimental		
Mg_3Al_1	3:1	3:1	82.18	21.89
KF/Mg_3Al_1	3:1	3:1	54.63	24.43
$Mg_3Al_{0.6}La_{0.4}$	3:0.6:0.4	3:0.6:0.3	53.14	20.96
KF/$Mg_3Al_{0.6}La_{0.4}$	3:0.6:0.4	3:0.6:0.3	21.86	24.90

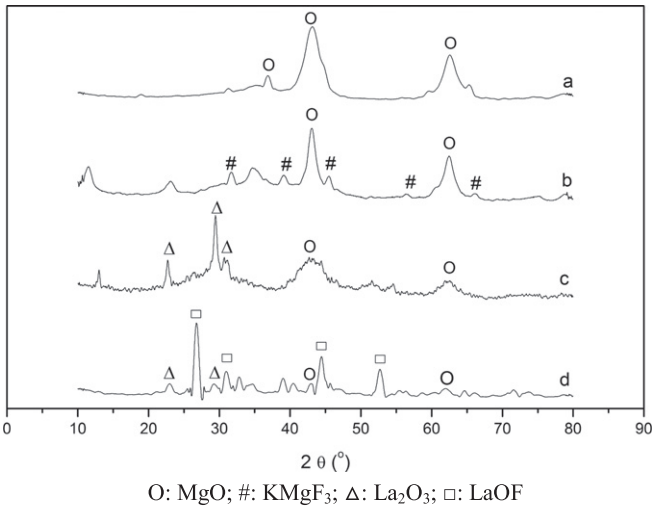

Fig. 1. XRD patterns of Mg_3Al_1 (a), KF/Mg_3Al_1 (b), $Mg_3Al_{0.6}La_{0.4}$ (c) and KF/$Mg_3Al_{0.6}La_{0.4}$ (d).

The location of F_{1s} levels are illustrated in Fig. 2. Three peaks in KF/Mg_3Al_1 spectra (a) were assigned to F^- anions of AlF_3 (687.6 eV), $KMgF_3$ (686.3 eV) and KF (684.0 eV). The replacement of Al^{3+} by La^{3+} in Mg_3Al_1 oxide led to disappearance of AlF_3 peak and appearance of LaOF (685.2 eV) peaks in KF/$Mg_3Al_{0.6}La_{0.4}$ spectra (b). According to the XRD results, the deposition of KF on precursor oxides surface led to fluorides. The Schottky defects resulted surface fluorine unsaturated.

The basicity of catalysts was characterized by CO_2-TPD, which is presented in Fig. 3. For Mg_3Al_1 oxide (a), there were three desorption peaks around 373 K, 473 K and 673 K, which was similar to the literatures [4, 6]. The three basic sites were OH^- groups (373 K), M-O pairs (473 K) and O^{2-} anions (673 K), respectively [21]. After KF specie was impregnated on Mg_3Al_1 oxide (b), there was a new significant desorption peak around 973 K, which indicated the increase of new basic sites. The new desorption peak around 973 K could be due to the unsaturated F^- anions according to XRD and XPS results. In the CO_2-TPD pattern of $Mg_3Al_{0.6}La_{0.4}$ oxide (c), the desorption peaks around 673 K became broad and intense after the substitution of Al^{3+} cations by La^{3+} cations. It was found that the basicity of oxides could be improved via La^{3+} cations modification [22]. Similarly, new broad desorption peaks appeared around 973 K in the CO_2-TPD pattern of KF/$Mg_3Al_{0.6}La_{0.4}$ oxide (d) after KF modification. The new adsorption peaks around 973 K could be due

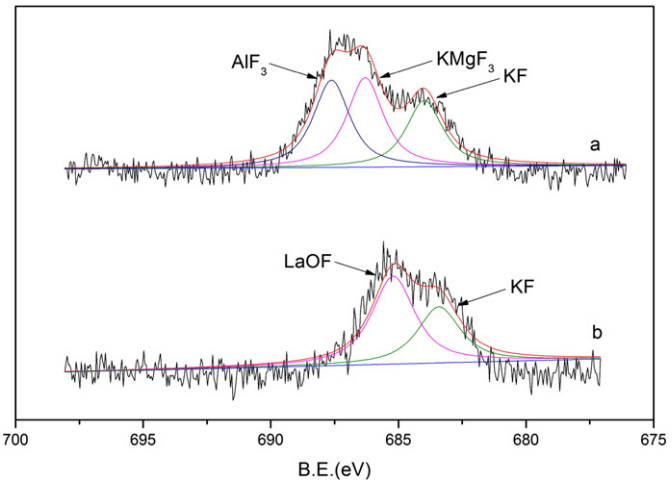

Fig. 2. XPS spectra of KF/Mg_3Al_1 (a) and KF/$Mg_3Al_{0.6}La_{0.4}$ (b) in the region of F_{1s} levels.