doi:10.1246/cl.2010.198

Transesterification of Triolein to Biodiesel Fuel over Mordenite-supported CaO Catalysts

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CaO catalysts supported on several metal oxides and zeolites were investigated for transesterification of triolein with methanol. Zeolite-supported CaO catalysts showed high catalytic activity for transesterification compared to the metal oxide-supported CaO catalysts; among the zeolites tested in this work, mordenite exhibited the best support. The catalytic activity of mordenite-supported CaO catalyst depended on both the amount of CaO loading and the calcination temperature for catalyst precursor.

Biodiesel fuel (BDF) is a promising non-toxic and biodegradable renewable alternative fuel comprised of fatty acid methyl esters derived from vegetable oil or animal fat. Methyl esters are usually produced by the transesterification of triglyceride with methanol.[1] The transesterification reaction has been reported to proceed efficiently in the presence of homogeneous base or acid catalysts.[2–6] Homogeneous base catalysts such as NaOH and KOH are potential candidates for use in the latest industrial processes for BDF production, due to faster reaction rates compared to the acid catalysts;[7] however, it is difficult to separate the homogeneous catalysts from the reaction solution.

A large number of heterogeneous base catalysts have been studied for the transesterification of vegetable oil to BDF: alkaline earth metal oxides and various alkaline metal compounds supported on alumina or zeolite.[8–16] In particular, calcium oxide (CaO), a heterogeneous base catalyst, has been widely studied for transesterification due to economical advantages.[14–16] By calcination in a helium gas flow, CaO was activated to match NaOH at catalyzing transesterification of soybean oil with refluxing methanol.[17] It is expected that supporting CaO on metal oxides with high surface area enhances the catalytic activity. However, there is little information about the catalytic activity of supported CaO catalysts for transesterification.[18] In this study, we investigated the catalytic activities of CaO catalysts supported on several metal oxides and zeolites for the transesterification of triolein with methanol to BDF.

An aqueous calcium acetate solution was impregnated on each support, followed by the calcination in vacuum at 500–900 °C for 1 h to obtain supported CaO catalysts (designated as CaO/support). The amount of CaO loaded on each support ranged between 0 and 40 wt %. As reference catalysts, commercial CaO calcined at 900 °C in vacuum and as-received $CaCO_3$ were used.

A 2.0-g portion of triolein, 0.05 g of catalyst, and 10 mL of methanol were added to a 100-mL flask under magnetic stirring at 500 rpm. Transesterification reactions were carried out at 50 °C for 0.5 h under N_2 atmosphere. After the reaction, the solid catalysts were removed by filtration. Products in the filtrate were fractionated and analyzed by GC-MS. The amount of methyl oleate ester was determined by comparison with that of 1-octanol as an internal standard. Catalytic activity was evaluated by the yields of methyl oleate ester (BDF yield), where the BDF yields were normalized by the weight of CaO loaded.

Table 1. BDF yields[a] and specific surface areas of supported CaO catalysts[b]

Catalyst	Calcination temp/°C	BDF yield $/\times10^{-2}$ mol (g-CaO)$^{-1}$	Specific surface area $/m^2$ (g-cat.)$^{-1}$
CaO/MOR	500	0	—[c]
	600	23.3	84.8
	700	25.5	55.6
	725	26.6	44.2
	750	31.7	40.2
	775	39.7	14.3
	800	19.7	12.6
	900	4.0	5.5
CaO/MFI	775	36.5	39.5
CaO/SiO_2–Al_2O_3	775	9.0	175
CaO/SiO_2	775	11.3	169
CaO/Al_2O_3	775	6.8	80.7
CaO	900	2.5	12.0
MOR	775	0	—[c]
$CaCO_3$	none	0	—[c]

[a]Reaction condition: catalyst (0.05 g), triolein (2.0 g), methanol (10 mL), 50 °C, 0.5 h. [b]CaO loading of supported catalyst was 30 wt %. [c]Not measured.

The BDF yields and the specific surface areas of supported CaO catalysts are summarized in Table 1, together with those of CaO and $CaCO_3$ reference catalysts. As shown in Table 1, the BDF yields of all the supported CaO catalysts calcined at 775 °C were higher than that of unsupported CaO reference catalyst calcined at 900 °C. Predictably, BDF yield was enhanced by supporting CaO on oxides with high surface area. BDF yields of the supported CaO catalysts calcined at 775 °C were dependent on the kind of supports and decreased in the following order: CaO/MOR > CaO/MFI $\gg$ CaO/SiO_2 > CaO/SiO_2–Al_2O_3 > CaO/Al_2O_3. The order of BDF yield was not in agreement with that of specific surface area, suggesting that the specific surface area is not the main parameter controlling catalytic activity. Among the supported CaO catalysts listed in Table 1, CaO/MOR exhibited the highest catalytic activity for transesterificaton of triolein with methanol to BDF. Therefore, the catalytic properties of CaO/MOR were studied in more detail.

The catalytic activity of CaO/MOR catalyst significantly depended on the calcination temperature of impregnated precursor, $(CH_3CO_2)_2Ca$/MOR, as shown in Table 1. No catalytic activity was observed for CaO/MOR calcined at 500 °C. When the CaO/MOR was calcined above 600 °C, BDF was produced. The BDF yield was most increased by catalyst calcined at 775 °C and drastically decreased by catalysts calcined at 800 and 900 °C.

Figure 1 shows in situ XRD patterns of $(CH_3CO_2)_2Ca$/MOR recorded at 600–900 °C under flowing N_2. When the sample was heated up to 600 °C, the diffraction peaks attributed

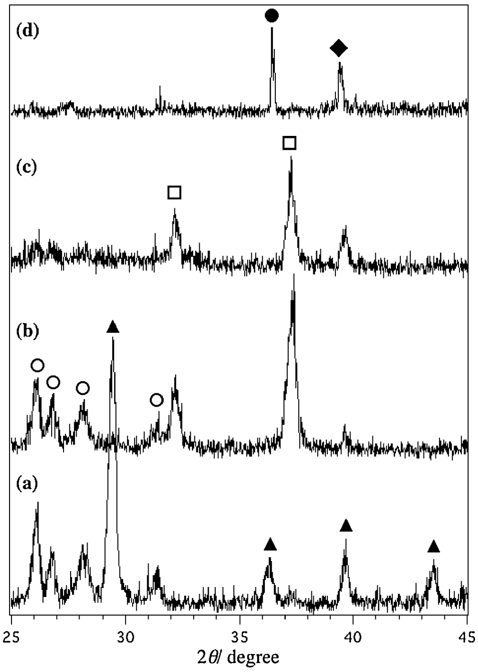

Figure 1. In situ XRD patterns of $(CH_3COO)_2Ca$/MOR heated at (a) 600, (b) 700, (c) 800, and (d) 900 °C. □, CaO; ▲, $CaCO_3$; ●, $CaSiO_3$; ◆, γ-$CaSiO_3$; and ○, MOR.

to $CaCO_3$ (▲) were clearly observed together with those to MOR zeolite (○). For the sample heated at 700 °C, the diffraction peaks due to $CaCO_3$ decreased and those assigned to CaO (□) were newly observed. The crystalline sizes of CaO on MOR were calculated from Scherrer's equation to be ca. 21 nm at 700–800 °C for diffraction line (200) of CaO. TG and TPD-MS measurements of $(CH_3CO_2)_2Ca$/MOR were carried out to examine the change in catalyst weight and the elimination from the catalyst, respectively, with increasing temperature. The TG result provided three steps of weight losses at <250, 350–550, and 600–750 °C, which correspond to the desorptions of H_2O, $(CH_3)_2CO$, and CO_2 from catalyst.[19,20] These desorption gases were confirmed by TPD-MS analysis. These results indicate that the calcium acetate supported on MOR was decomposed to CaO at ca. 600 °C via $CaCO_3$ generated by release of $(CH_3)_2CO$ from $(CH_3CO_2)_2Ca$ [$(CH_3CO_2)_2Ca \rightarrow CaCO_3 + (CH_3)_2CO$].

As shown in Table 1, $CaCO_3$ was inactive for BDF synthesis. Therefore, no catalytic activity of catalyst calcined at 500 °C could be ascribed to the formation of $CaCO_3$. The sample calcined at 700–800 °C contains CaO particles active for transesterification, formed by the desorption of CO_2 from $CaCO_3$. As can be seen in Figure 1d, when the CaO/MOR catalyst was heated at 900 °C, XRD diffraction peaks assigned to MOR completely disappeared, indicating the destruction of the zeolitic crystalline structure. It should be noted that the XRD peaks assigned to CaO also disappeared and that other peaks assigned to $CaSiO_3$ derivatives appeared.[21,22] This indicates that supported CaO reacted with tetrahedral SiO_2 in the zeolite framework. From these results, a significant decrease in catalytic activity of CaO/MOR calcined at 900 °C is considered to be due to the decrease in the number of CaO active sites by the agglomeration and/or the reaction of CaO and the destruction of zeolite crystalline structure.

The BDF yields of MOR-supported CaO catalysts calcined at 775 °C with different CaO load were also investigated. Na-MOR without CaO exhibited no catalytic activity (Table 1), supporting our statement that CaO acts as the active site for transesterification of triolein. Catalytic activity was low for CaO/MOR catalyst with 10 wt % CaO loading. Maximal activity was achieved for CaO/MOR catalyst with 30 wt % CaO loading. When the amount of CaO loading was further increased, the catalytic activity drastically decreased. This may be due to the aggregation of CaO particles. A similar result has been reported by Xie et al.[23]

Catalytic activity for transesterification has been reported to be dependent on basicity; the stronger the basicity, the higher the activity.[8,9,11] Arishtirova and co-workers reported that the basicity of BaO supported on zeolite changed according to the type of zeolite support used and that the MOR-supported BaO showed the strongest basicity.[24] Considering the above literature, CaO/MOR catalyst may have the strong basicity, resulting in the high catalytic activity for transesterification. Further study is required.

We first demonstrated that the zeolite-supported CaO catalysts, especially CaO/MOR calcined at 775 °C, exhibited the best performance for transesterification of triolein with methanol to BDF among several metal oxide- and zeolite-supported CaO catalysts. The stabilities of supported CaO catalysts are under investigation.

We thank Professor Dr. Koichi Eguchi and Dr. Hiroki Muroyama, Kyoto University, for permission and support to use the in situ XRD equipment.

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