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Catalysis Communications



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Short communication

Production of diethyl carbonate from ethylene carbonate and ethanol over supported fluoro-perovskite catalysts



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ABSTRACT

ARTICLE INFO

The KCaF₃/C (K-Ca(A)) catalyst was shown to be effective as heterogeneous basic catalysts for the transesterification of ethylene carbonate (EC) and ethanol among fluoro-perovskite (XYF₃)/C (X = K, Cs, Y = Mg, Ca) catalysts. Although the KMgF₃/C (K-Mg (A)) catalyst exhibited the highest catalytic activity among the XYF₃/C catalysts studied, the potassium leaching was observed on K-Mg (A). CO₂ temperature programmed desorption (TPD) revealed that the superior catalytic activity of the XYF₃/C was due to its strong basic sites. CO₂-TPD and XPS measurements indicated that strong basic sites are generated by an increase in the electron density of fluorine.

1. Introduction

Keywords:

Fluoro-perovskite

Transesterification

Diethyl carbonate

Diethyl carbonate (DEC) has been applied as a solvent for paint and fragrances, the electrolyte in Li-ion batteries, and as an ethylization or carbonylation reagent in organic synthesis [1–3]. DEC has also received attention as an oxygen-containing fuel additive [3–5]. The transesterification of ethylene carbonate (EC) and ethanol (Eq. (1)) for the production of DEC is an environmentally harmonized process because the EC reactant is produced through the reaction of ethylene oxide and carbon dioxide, which is a greenhouse gas (Eq. (2)) [2,6].

$$\begin{array}{c} 0 \\ 0 \end{array}^{0} + 2 \end{array}^{0} OH \longrightarrow 0 \\ 0 \end{array}^{0} \begin{array}{c} 0 \\ 0 \end{array}^{0} + H 0 \\ (1) \end{array}^{0} OH$$

$$\underline{\wedge} + co_2 \longrightarrow \bigcirc_0^{\circ} \bigcirc_0^{\circ}$$
 (2)

Basic catalysts are effective for catalyzing the transesterification reaction. Various solid basic catalysts have been reported for this purpose, including alkaline earth metal oxides [7–13], polymer resins [14], and basic zeolites [15], because the separation and recovery of these catalysts is easier than that of conventional homogeneous basic catalysts. Among them, alkaline fluorides are an attractive choice due to their high catalytic activity in transesterification reactions [2,6,12,16,17]. For instance, we recently reported that supported fluoro-perovskite catalysts, which are prepared by an impregnation method, are effective for the transesterification of an edible oil doped with fatty acids and methanol [18].

A mechano-chemical technique has been often used for various complexes synthesis at lower temperature [19–21]. The application to supported catalyst preparation is expected to highly disperse active component. Therefore, the present study was applied the mechano-chemical treatment to the preparation of supported fluoro-perovskite catalysts.

The purpose of the present study was to explore the effects of the alkali and alkali earth metals and catalyst preparation procedure on the catalytic performance of activated carbon-supported fluoro-perovskite (XYF₃/C, X = K, Cs, Y = Mg, Ca) catalysts during the transesterification of EC and ethanol.

2. Experimental

Supported fluoro-perovskite catalysts were prepared using a mechano-chemical method. Activated carbon (FY-1, Cataler, $S_{BET} = 800 \text{ m}^2 \text{ g}^{-1}$), SiO₂ (Q-6, Fuji Silysia, $S_{BET} = 275 \text{ m}^2 \text{ g}^{-1}$), or Al₂O₃ (JRC-ALO-6, a reference catalyst of the Catalysis Society of Japan, $S_{BET} = 161 \text{ m}^2 \text{ g}^{-1}$) was used as the support. Alkaline fluoride (XF, where X = K, Cs) and alkaline earth hydroxide (Y(OH)₂, where Y = Mg, Ca) were combined with the support powder and zirconia balls in zirconia vessels. In the case of an unsupported KMgF₃ catalyst, KF and Mg(OH)₂ were combined with zirconia balls in zirconia vessels. The molar ratio of the alkaline metal to the alkaline earth metal was 3:1. The molar amount of the alkaline earth metal relative to the support powder was 20 mmol $g_{support}^{-1}$. The zirconium vessels were placed in a planetary ball mill (Frisch, P-7), and the mechano-chemical treatment was performed at a rotation rate of 800 rpm for 30 min. As shown in the

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https://doi.org/10.1016/j.catcom.2018.01.019

Received 22 September 2017; Received in revised form 13 January 2018; Accepted 15 January 2018 1566-7367/ © 2018 Elsevier B.V. All rights reserved.

Fig. 1. XRD profiles of as-prepared catalysts.





Fig. 2. Catalytic activities of XYF₃/C catalysts.

XRD profile of K-Mg(A) after the milling process (Fig. S1), the desired fluoro-perovskites were formed during this step according to the following equation,

$$3XF + Y(OH)_2 \rightarrow XYF_3 + 2 XOH$$
 (3)

In order to eliminate the alkaline hydroxide byproduct from the catalyst, the material obtained from the mechano-chemical treatment was washed three times with methanol and then dried at 373 K for 12 h, and finally calcined at 773 K for 1 h in a stream of N_2 (termed catalyst (A)). In addition, the K-Mg catalyst was also prepared with the calcination and washing steps reversed (termed catalyst (B)). The flowcharts for the both preparation procedures were described in supplementary material (Fig. S2).

The transesterification of EC was performed using a batch reactor. The reaction conditions were as follows: 10 mmol of EC, 400 mmol of ethanol, 0.5 g of catalyst (0.57 $g_{-cat} g_{-EC}^{-1}$ of the amount of catalyst to EC), reaction temperature of 343 K. The amounts of reactants and products were determined using a flame ionization detector/gas

chromatograph (FID-GC; DB-1 capillary column, 60 m, 0.52 mm i.d., GC-14B, Shimadzu). The DEC yield was defined as:

DEC yield = molar amount of DEC formed/molar amount of EC charged

(4)

To examine the reusability of catalyst, 2nd run test was performed. After the 1st run test, the catalyst was separated from the reaction solution by filtration, the separated catalyst was washed with ethanol and then dried at 373 K, calcined at 773 K. the resultant material was used to the 2nd run test.

The Brunauer-Emmett-Teller (BET) surface areas of the newlyprepared 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 N_2 : 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 Ka radiation. The size of fluoride crystallites was calculated using the Scherrer equation. CO₂ temperature programmed desorption (TPD) measurements were carried out with a pulse reactor in conjunction with a mass spectrometer (M-200GA-DM, Canon Anelva) to detect desorbed carbon dioxide at m/z = 44. Catalyst samples were pretreated at 773 K for 1 h in a stream of helium. After cooling, carbon dioxide was adsorbed on the catalysts at ambient temperature and CO₂-TPD data were acquired at a heating rate of 10 K min⁻¹ in a steam of helium up to a maximum temperature of 1073 K. X-ray photoelectron spectroscopy (XPS) was performed using a Quantum 2000 (Ulvac Phi) instrument with an Al anode, a beam diameter of 100 µm and an acceleration voltage of 15 kV. Leaching tests for alkaline metal were carried out with an atomic absorption spectrometry (AAS; AA-7000, Shimadzu). Absorption wavelengths for K and Cs were 767 nm and 827 nm, respectively. After the separation of catalyst by the filtration, the alkaline metal concentration in the reaction solution was analyzed.

3. Results and discussion

As shown in Fig. S3, K-Ca(A)/C (Activated carbon) exhibited the highest catalytic activity among the supported K-Ca (A) catalysts. In addition, the catalytic activity of K-Mg (A)/C was higher than that of unsupported K-Mg (A) catalyst (Fig. S4). Hereinafter, the activated carbon was used as the support. As shown in Fig. 1, diffraction peaks



Fig. 3. CO2-TPD profiles of as-prepared and used catalysts: (A) as-prepared, (B) used.



Fig. 4. Relationship between DEC yield and strong basic site density of catalysts (1st and 2nd).

assignable to KMgF₃ (perovskite, JCPDS 18-1033) were observed for K-Mg (A), whereas peaks assignable to K₂MgF₄ (layered perovskite-like, JCPDS 23-0469) were observed for K-Mg (B). In addition, the formation of MgO as a byproduct was observed for both catalysts. The difference in the washing and calcination procedure during the catalyst preparation greatly affected the crystalline structure of the K-Mg fluoride. The residual potassium probably caused the transition from a perovskite structure to a layered perovskite-like structure during the calcination. In the case of the K-Ca (A) and Cs-Ca (A) catalysts, peaks assignable to a perovskite structure were observed for the K-Ca (A) and Cs-Ca (A) catalysts together with the peaks assignable to CaF_2 (JCPDS 35-0516). The formation of CaF_2 would be attributed to the loss of some of the $XCaF_3$ (X = K, Cs) perovskite from the catalysts via leaching of potassium during the washing step after the milling. The BET surface area and crystallite size of fluoride of the prepared catalysts were shown in Fig. 1. The BET surface area was increased in the following order: Cs-Ca

(A) < K-Mg(A) \ll K-Ca (A) < K-Mg (B), whereas the crystallite size of fluoride was increased in the following order: K-Mg (A) < K-Mg (B) < Cs-Ca (A) < K-Ca (A). The relationship between the both was not confirmed, although the supported active component dispersion was generally increased with an increase in the surface areas of catalyst.

Fig. 2 shows the catalytic activities of the K-Mg (A, B), K-Ca (A), and Cs-Ca (A) catalysts for transesterification of EC and ethanol. By the way, another product was not detected except for DEC and ethylene glycol as products for transesterification (Eq. (1)). Therefore, the selectivity for DEC was 100% and the conversion of EC is equal to the yield of DEC. The catalytic activity K-Mg (A) with a perovskite structure was remarkably higher than that of K-Mg (B) with a layered perovskite-like structure. Although the formation of MgO was observed for K-Mg (A and B) in Fig. 1, the DEC yield for MgO/C (5.3% @ 6 h.) which was prepared using Mg (OH)₂ only, was smaller than those for K-Mg (A and B). This result indicates that MgO little contribute to the reaction. The catalytic activity of XYF₃/C with perovskite structure decreased in the following order: K-Mg > Cs-Ca > K-Ca. The order of the catalytic activity agreed with the order of crystallite size of fluoride, not relating to the BET surface area. This indicates that the fluoride dispersion affects to the catalytic activity.

Fig. 3 (A) shows the CO₂-TPD profiles of as-prepared catalysts. Desorption peaks assignable to strong basic sites (S peak) were observed at temperatures over 750 K. and desorption peaks assignable to weak basic sites (W peak) were observed at temperatures below 750 K. As shown in Fig. 3(A), the total amounts of CO₂ desorbed on the as-prepared catalysts were increased in the following order: Cs-Ca (A) = K-Ca (A) < K-Mg (B) < K-Mg (A). This indicates that the total number of basic sites do not relate to the catalytic activity so much. Fig. 4 shows the relationship between the catalytic activity and number of strong basic sites. The DEC yields for XYF₃/C almost correlated to the number of strong basic sites. Whereas the K-Mg (B) with layered perovskite like structure did not agree with the correlation for XYF₃/C. The difference of catalytic activity between perovskite and layered perovskite like structures cannot explained by the number of strong basic sites. Fig. 5 shows the XP spectra of as-prepared and used catalysts. As shown in Fig. 5, the binding energy for F1s of as-prepared catalyst was decreased in the following order: K-Ca (A) > K-Mg (A), K-Mg (B) > Cs-Ca (A). The shift toward to lower energy indicates an increase in the electron density of fluorine. As shown in Fig. 3 (A), the peak temperature of

Fig. 5. XP spectra of as-prepared and used catalysts.



Table 1
Catalyst reusability and leaching of alkaline metals.

Catalyst	DEC yield/% ^a			Concentration of alkaline metals in reaction solution
	1st	2nd	2nd/1st	/wt%
K-Mg (A)	78.1	76.4	0.98	0.22
K-Ca (A)	64.3	73.1	1.14	0.09
Cs-Ca (A)	72.7	54.9	0.76	0.47
K-Mg (B)	32.6	23.1	0.71	0.02
KF/C	69.2	2.3	0.03	0.41

^a Reaction time: 6 h.

main S peak (the largest peak among S peaks) was increased with in the following order: K-Ca (A) (855 K) < K-Mg (A) (865 K), K-Mg (B) (880 K) > Cs-Ca (A) (952 K). There is a correlation between the shift

of binding energy for F1s and the peak temperature of main S peak. Therefore, the strong basic site would be generated by an increase in the electron density of fluorine. The strong Lewis basic site would be assigned to active sites for the reaction based on the correlation in Fig. 4. Catalyst reusability and leaching of alkaline metals in the reaction solution were summarized in Table 1. It is clear from Table 1 that XYF₃/C exhibited superior reusability compared to KF/C, although leaching of alkaline metal was confirmed. The catalytic activity of K-Mg (A) in the 2nd run was slightly lower than that in 1st run. The catalytic activity of K-Ca (A) was increased in the 2nd run. Fig. 3 (B) shows the CO₂-TPD profiles of used catalysts (after 1st run). As shown in Fig. 3 (B), the strong basic site density on the K-Mg (A), K-Mg (B), and Cs-Ca (A) catalysts decreased as a result of after the 1st run. The percentage decrease of strong basic sites increased in the following order: K-Mg (A) (16.2%) < Cs-Ca (A) (19.6%) < K-Mg (B) (24.0%). In contrast, the strong basic site density on K-Ca (A) increased as a result of the reaction (by 23.5%). The variation of catalytic activity between 1st and 2nd runs

of K-Ca (A) agrees with the variation of strong basic site density of CO₂-TPD and the peak shift of F1s of XP spectra. In addition, there are also a correlation between the DEC yield at 2nd run and strong basic site density as shown in Fig. 4. Although the details are unknown, the strong basic site density was increased by the change in the structure during the reaction, resulting in an increase in the catalytic activity of K-Ca (A). The concentration of alkaline metals in the reaction solution was increased in following order: K-Mg(B) < K-Ca (A) < K-Mg(A) < KF/ C < Cs-Ca (A) as shown in Table 1. In contrast, it is clear from Fig. 5 that the peak intensities for K 2p, and F1s, and Mg 2p (or Ca 2p) changed little as a result of the reaction in the cases of the K-Mg (A). K-Mg (B), and K-Ca (A) catalysts, although the peak intensities for Cs 3d5/ 2. Ca 2p. and F1s of the Cs-Ca (A) decreased remarkably as a result of the reaction. This result indicates that most of alkaline metal was reinsured on K-Mg (A, B) and K-Ca (A). From the above facts, K-Ca (A) was indicated to exhibit superior catalytic activity and reusability, resistance against alkaline metal leaching.

4. Conclusion

 $KCaF_3/C$ catalyst were found to be relatively effective as heterogeneous catalysts for the transesterification of EC and ethanol compared to KF/C. Although K-Mg (A) had superior catalytic activity among the XYF₃/C catalysts studied, the potassium leaching is remarkably observed in the reaction solution.

There is a correlation between the DEC yield and the strong basic site density of XYF₃/C catalysts. Therefore, the strong basic sites were indicated to contribute to the catalytic activity for transesterification of EC. In addition, the shift of the binding energy for F1s was correlated to the peak intensity of CO_2 desorbed at the highest temperature. Therefore, the strong basic site would be generated by the electron donation from alkaline metal to fluorine.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2018.01.019.

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