Production of Diethyl Carbonate from Ethylene Carbonate and Ethanol over Supported Fluoro-perovskite Catalysts

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Abstract: Activated carbon-supported fluoro-perovskite catalysts was shown to be effective as heterogeneous basic catalysts for the transesterification of ethylene carbonate and ethanol. The $KMgF_3/C$ (K-Mg) exhibited the highest catalytic activity and the $KCaF_3/C$ (K-Ca) exhibited superior reusability among the fluoro-perovskite catalysts prepared. The CO_2 temperature programmed desorption (TPD) and XPS measurements revealed that the superior catalytic activity of fluoro-perovskite was due to its strong basic sites and the strong basic sites were generated by an increase in the electron density of fluorine.

Keywords: Fluoro-perovskite, heterogeneous basic catalysts, transesterification.

1. Introduction

The transesterification of ethylene carbonate (EC) and ethanol for the production of diethyl carbonate (DEC), which is applied as solvents for paint and fragrances, electrolytes in Li-ion batteries, and ethylization or carbonylation reagents in organic synthesis, is an environmentally harmonized process because the EC reactant is produced through the reaction of ethylene oxide and carbon dioxide. Basic catalysts are effective for catalyzing the transesterification reaction. Various solid basic catalysts have been reported for this purpose. Among them, alkaline fluorides are an attractive choice due to their high catalytic activity in the reactions. We recently reported that supported fluoro-perovskite catalysts are effective for the transesterification of an edible oil contained with free fatty acids and methanol[1]. The purpose of the present study was to explore the effect of the alkali and alkali earth metals on the catalytic performance of activated carbon-supported fluoro-perovskite catalysts (XYF_3/C: XYF_3, 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) 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 zirconium balls in zirconia vessels (20 $\text{mmol}_{\text{-alkaline earth metal}}\ \text{g}_{\text{support}}^{-1}$). The mechano-chemical treatment was performed at a rotation rate of 800 rpm for 30 min using a planetary ball mill (Frisch, P-7). The desired fluoro-perovskites were formed during this step. 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. 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, reaction temperature of 343 K, reaction time of 6 h. After the 1st run test, the separated catalyst was washed with ethanol and then dried at 373 K, calcined at 773K. the resultant material was used to the 2nd run test. The CO_2-TPD measurements were carried out with a pulse reactor in conjunction with a mass spectrometer to detect desorbed carbon dioxide at m/z = 44. CO_2-TPD data were acquired at a heating rate of 10 K min^{-1} in a steam of helium up to maximum temperature of 1073 K.

3. Results and discussion

Figure 1 shows the CO_2-TPD profiles of as-prepared XYF_3/C catalysts. The desorption peaks at the temperature over 750 K assigned to the strong basic sites (S peak) and the desorption peaks at the temperature below 750 K assigned to the weak basic sites (W peak) were observed. The total amount of CO_2 adsorbed on K-Mg was the largest among the XYF_3/C catalysts. The ratio of S peak to W peak on Cs-Ca was larger than that on K-Ca, although the total number of basic sites on Cs-Ca was almost the same as K-Ca. As can be seen in Figure 2, the DEC yield (1st run (as prepared)) for XYF_3/C decreased in the following order: K-Mg > Cs-Ca > K-Ca. In addition, the DEC yield for K-Mg in the 2nd run (after 1st run) was slightly lower than that in 1st run, whereas the DEC yield for Cs-Ca in the 2nd run was remarkably lower than that in 1st run. In contrast, the DEC yield for K-Ca was increased in the 2nd run. The binding energy for F1s of used K-Ca (685.8 eV) was lower than that of as-prepared K-Ca (686.9 eV) in the XP spectra. This indicates the increase in Lewis basicity due to some kind of structural change.

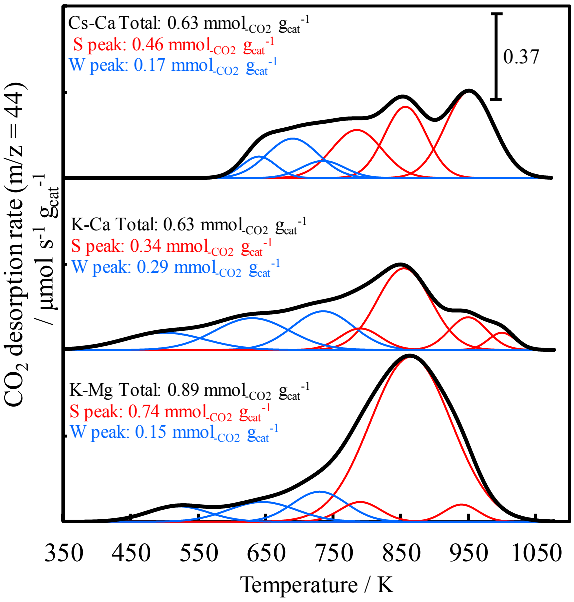

Figure 1. CO_2-TPD profiles of as-prepared XYF_3/C catalysts.

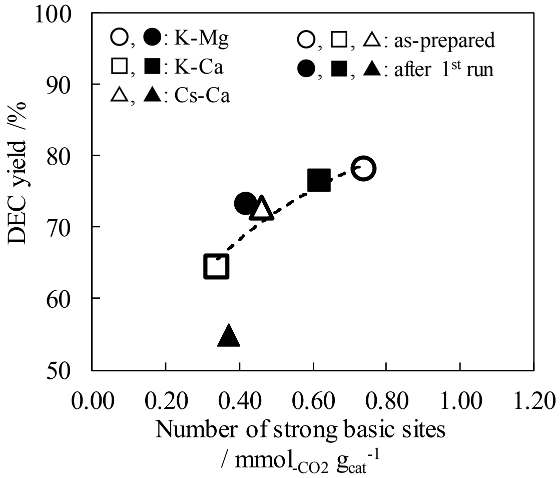

Figure 2. Relationship between the DEC yield and number of strong basic sites.

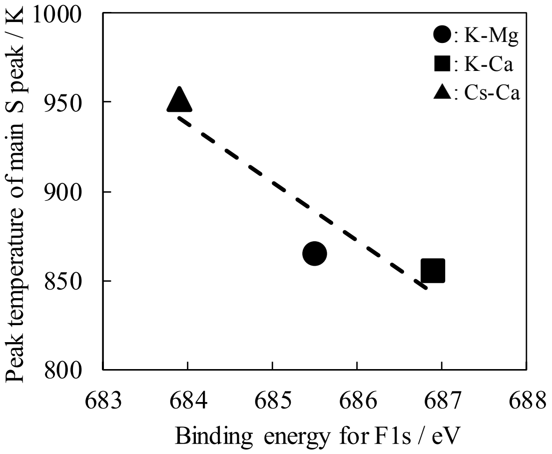

Figure 3. Relationship between the strength of strong basic sites and the binding energy for F1s.

Furthermore, the DEC yields for XYF_3/C (1st and 2nd runs) basically correlated to the number of strong basic sites, as shown in Figure 2. The number of strong basic sites on used K-Ca was much than that of as-prepared K-Ca, correlating to the DEC yields. This indicates that the strong basic sites were mainly contributed to the catalytic activity for transesterification of EC and that the reason for catalyst deactivation is a decrease in the number of strong basic sites. Figure 3 shows the relationship between the strength of basicity (peak temperature) of main S peak (the strongest peak among S peaks) and the binding energy for F1s. There is a correlation between the both. Therefore, the strong basic site would be generated by an increase in the electron density of fluorine.

4. Conclusions

Activated carbon supported fluoro-perovskite catalysts were found to be effective as heterogeneous catalysts for the transesterification of EC and ethanol. The CO_2-TPD and XPS measurements revealed that the strong basic sites were indicated to contribute to the catalytic activity for transesterification of EC and the strong basic site was generated by an increase in the electron density of fluorine.

References

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