Investigation of active species on lanthanum catalysts in the ketonization of carboxylic acids

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Abstract: Ketonization of propanoic acid, hexanoic acid, and octanoic acid were performed over La_2O_3 catalyst at a temperature between 325 °C and 425 °C. During the reaction, the catalyst was transformed into other compounds such as $La_2O(RCOO)_4$ (< 350 °C) and $La_2O_2CO_3$ (>350 °C). We found that the reaction order was zero and Arrhenius plot for the ketonization shows liner correlation within the all reaction temperature between 325 and 425 °C irrespective of the difference in the crystal structure. These results mean that activation process of carboxylic acids in the ketonization reaction is not affected by the difference in the crystal structure of catalyst.
Keywords: Ketonizetion, Carboxylic acid, Crystal structure.

1. Introduction

The formation of ketone from two carboxylic acid molecules, which is called ketonization reaction, has been widely studied. Many studies suggest that among various metal oxides those with amphoteric and/or redox natures such as TiO_2, CeO_2, and ZrO_2 are more active for the ketonization than others. Recently, we investigated vapor-phase ketonization of acetic acid over La_2O_3 and found that La_2O_3 was one of the most active catalysts for the ketonization[1]. In addition, catalytic activity of La_2O_3 at 350 °C was higher than those at 375, 400, and 425 °C. We estimated that La_2O_3 transformed into $LaO(CH_3COO)$ in ketonization of acetic acid at 350 °C[1], and proposed that $LaO(CH_3COO)$ shows higher activity than La_2O_3. However, relationship between structure of transformed compounds and catalytic activity have not been studied in detail. Various carboxylic acids have been applied to catalytic ketonization. It is necessary to clarify what occurs in the ketonization of carboxylic acids other than acetic acid. In this work, we carried out the ketonization of carboxylic acids such as propanoic acid, hexanoic acid, and octanoic acid over La_2O_3 catalyst. From the structural change in catalyst during the catalytic reaction as well as the reaction kinetics, we clarified the effect of the change in the crystal structure of La-compounds on activation process of carboxylic acids.

2. Experimental

Carboxylic acids were purchased from Wako Pure Chemical Industries, Ltd., Japan, and were used as raw materials in the catalytic reactions without further purification. A La_2O_3 purchased from Kanto Chemical Co. Japan was used as a catalyst after calcination at 1000 °C for 2h in order to desorb CO_2. Catalytic reactions were carried out in a conventional fixed-bed down flow reactor under an atmospheric pressure of N_2 flow (30 cm^3min^{-1}) and a temperature of 325–425 °C. In each test, La_2O_3 was loaded into the reactor. The catalyst was heated under N_2 flow at 500 °C for 1h. After the catalyst had been cooled to a reaction temperature between 325 °C and 425 °C, carboxylic acid was fed through the top of the reactor together with N_2 flow of 30 cm^3min^{-1}. Typical reaction condition was the following: the catalyst weight (W), 0.5 g; the feed rate (F), 4.3 $cm^3\ h^{-1}$.

3. Results and discussion

In the ketonization of propanoic acid, the conversion monotonically increases from ca. 6 to 74% with increasing reaction temperature from 325 °C to 425 °C, whereas the selectivity to 3-pentanone maintains high values around 100% within the temperature range. In the ketonization of hexanoic acid and octanoic acid, 6-undecanone and 8-pentadecanone were obtained with high selectivity, respectively. In case of the

ketonization of acetic acid, catalytic activity at 350 °C had achieved the highest value within the temperature range from 325 to 425 °C[1]. This trend do not appear in the ketonization of other carboxylic acids. Fig. 1 shows XRD patterns of La_2O_3 and La-catalysts after ketonization of propanoic acid at each reaction temperature. Most of La_2O_3 catalyst is transformed into a layered structure after ketonization at 325°C. La_2O_3 crystal phase tends to remain at high reaction temperature ≥ 375 °C. In addition, a new phase characterized with three peaks at 12.9°, 30.9° and 44.8° are observed in the La-catalyst at ≥ 375 °C. CHN analysis and TG-DTA results suggest that the catalyst was transformed into other compounds such as $La_2O(CH_3CH_2COO)_4$ (< 350 °C) and $La_2O_2CO_3$ (>350 °C) during the ketonization. During ketonization of hexanoic acid and octanoic acid, La_2O_3 catalysts also transformed $La_2O(RCOO)_4$ and $La_2O_2CO_3$. In order to clarify the reaction order in the ketonization of carboxylic acids, we carried out ketonization over La_2O_3 at different contact time (*W*/*F*). Based on the result, we conclude the ketonization follows the zero-order kinetics. Fig. 2 shows Arrhenius plots for the ketonization reaction using zero-order reaction rate constants. Arrhenius plots show liner relation between 325 and 425 °C irrespective of the difference in the crystal phase of the catalyst. This result suggests that the difference in crystal phases between $La_2O(RCOO)_4$ and $La_2O_2CO_3$ have little influence on activation process.

4. Conclusions

Ketonization of carboxylic acid was carried out at 325, 350, 375, 400, and 425 °C with La_2O_3 catalyst. La_2O_3 catalyst transformed into other compounds e.g. $La_2O(RCOO)_4$ and $La_2O_2CO_3$ depending on reaction temperature. However, reaction mechanism and number of active sites for the ketonization probably similar to each other regardless of reaction temperature and crystal structure of the catalysts.

References

1. Y. Yamada, M. Segawa, F. Sato, T. Kojima, S. Sato, J. Mol. Catal. A: Chem. 346(2011) 79.

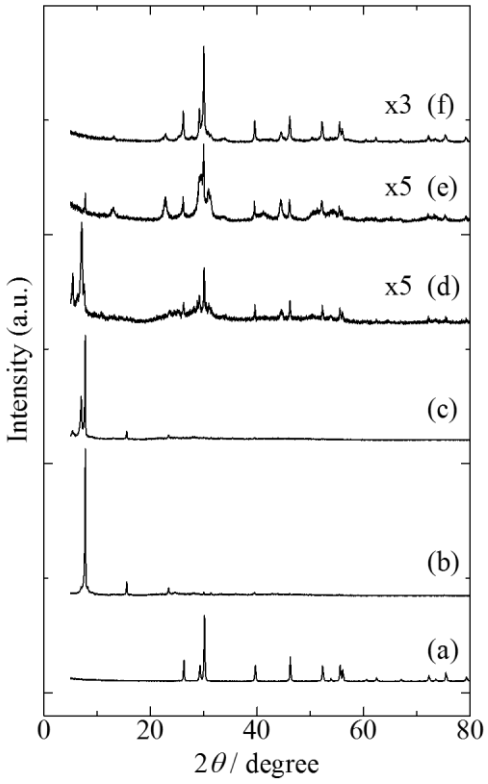

Figure 1. XRD patterns of (a) La_2O_3 calcined at 1000 °C for 2h and La-catalysts after used in ketonization of propanoic acid at (b) 325 °C, (c) 350 °C, (d) 375 °C, (e) 400 °C, and (f) 425 °C.

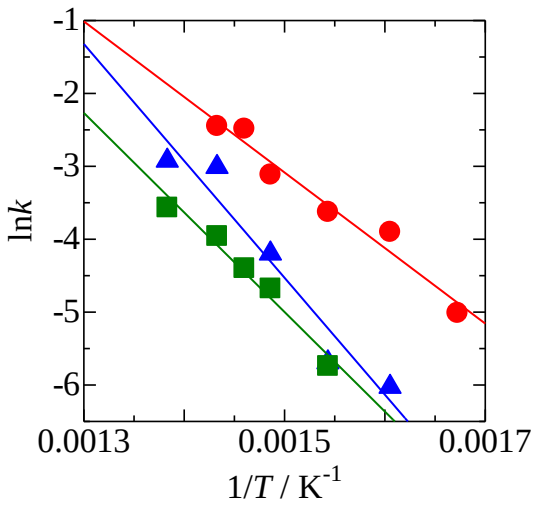

Figure 2. Arrhenius plots for the ketonization of (circle) propanoic acid, (triangle) hexanoic acid, and (square) octanoic acid over La_2O_3: *k* is zero-order reaction rate constant.