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The oxidative dehydrogenation of ethane over alkali-doped lanthanum–calcium oxide catalysts

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The oxidative dehydrogenation of ethane has been investigated over Li-, Na- and K-doped La/CaO catalysts at temperatures of 550–650°C. The addition of alkali metals to La/CaO increases the ethylene selectivity. For Li- and Na-doped La/CaO catalysts, the ethane conversion remains almost unaltered. The increase of ethylene selectivity over the two catalysts is believed to be mainly caused by coordinative action of lithium and lanthanum or sodium and lanthanum. However, the Li-doped La/CaO catalyst exhibits stronger coordinative action than the Na-doped La/CaO catalyst. Catalyst characterization reveals that the strong coordinative action of components in Li/La/CaO is probably related to the chemical and crystal structure of the catalyst which is favorable for oxidative dehydrogenation of ethane. The results also show that addition of potassium, being a poor dopant, to La/CaO results in a sharp decrease in catalytic activity.

Keywords: ethane; oxidative dehydrogenation; lanthanum–calcium oxide; catalysts; alkali promotion

1. Introduction

The catalytic oxidative dehydrogenation of ethane to ethylene has become important only in the last decade [1–6]. The oxidative coupling of methane to higher hydrocarbons has been intensively investigated with the discovery of ever more large resources of natural gas. Research on ethane oxidation is of value since ethane is the second major component of natural gas and also a main product in many methane coupling reactions. The transformation of ethane to products such as ethylene and acetaldehyde has applications to commercial materials. In addition, ethane oxidation may be useful for understanding other oxidation processes such as that involving methane.

A wide variety of solids has been examined as catalysts for the oxidative dehydrogenation (ODH) of ethane. Molybdenum–vanadium oxide catalysts have been largely studied [7–10]. Li/MgO is another type catalyst that is intensely investigated for the ethane oxidation [11–14]. Morales and Lunsford [11] found that although Li/MgO catalyst is effective for both oxidative coupling of methane and oxidative dehydrogenation of ethane, the reaction of ethane oxidation was faster than that of methane oxidative coupling. The mechanism of the two reactions is somewhat different. Research on other types of catalyst for ethane oxidation was also reported [15,16]. A new class of oxide catalysts developed for oxidative dehydrogenation of ethane in our laboratory opens a promising field of catalyst investigation. This paper reviews the performance of lanthanum–calcium oxides doped with Li, Na or K in the ODH of ethane. Our results reveal the effect of addition of dopants to La/CaO catalysts on catalytic activity and ethylene selectivity. Among the alkali-doped oxides, the lithium-doped lanthanum–calcium catalyst is the most favorable for the ODH reaction of ethane. We studied the influence of lithium content of Li-doped La/CaO catalyst on reactivity in detail. The role of lithium in Li/La/CaO catalyst is proposed on the basis of our research. The superior behaviour of Li-doped La/CaO catalyst for the ODH of ethane is satisfactorily explained.

2. Experimental

2.1. Catalyst preparation

The La/CaO catalyst was prepared by means of precipitation. Calcium hydroxide powder was added to a solution of lanthanum nitrate. The precipitate was filtered and dried overnight at 120°C. La/CaO catalysts doped with Li, Na or K were prepared by wet mixing. The La/CaO precipitate was added to lithium, sodium and potassium nitrate solution respectively. Each wet mixture was stirred and heated to evaporate the water. The obtained paste was dried overnight at 120°C. The Li/CaO catalyst was prepared by impregnation in aqueous solution. Calcium oxide powder was added to a stirred lithium nitrate solution. The formed slurry was heated to obtain a thick paste that was dried overnight at 120°C. All the dried samples were calcined in air at 600°C for 10 h.

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Table 1
The performances of La / CaO catalysts at some Li / La ratios for oxidative dehydrogenation of ethane at 600°C

Atom ratio La : Ca	Conversion of C_2H_6 (%)	Product selectivity (%)				Yield of C_2H_4 (%)
		CO	CO_2	CH_4	C_2H_4	
0.1	39.2	0	29.3	0	70.7	27.7
0.2	44.7	0	23.6	0	76.4	34.2
0.4	48.8	0	25.0	0	75.0	36.6
0.6	45.9	0	28.7	0	71.3	32.7
0.8	42.2	0	32.9	0	67.1	28.3
1.0	41.7	0	36.1	0	63.9	26.6
1.2	40.6	0	45.8	0	54.2	22.0
Ca-free	38.3	0	56.4	0	43.6	16.7

2.2. Catalyst testing

The catalytic activity measurements were carried out in a fixed-bed continuous flow quartz microreactor at atmospheric pressure. The reaction temperature ranged from 550 to 650°C. In this temperature range, the homogeneous reaction was checked and found to be negligible. The feed consisted of 15.2 vol% ethane, 8.6 vol% oxygen and 76.2 vol% nitrogen with space velocity of 1000 h^{-1} (GHSV at STP). The products were analysed by a gas chromatograph equipped with Porapak Q and 5A sieve columns.

2.3. Catalyst characterization

The surface areas of the catalysts were measured using the BET method with krypton as the adsorbate.

X-ray diffraction analyses were carried out on a Rigaku D / MAX-RB diffractometer. The radiation used was Cu Kα with a Ni filter.

Thermal analyses of the catalysts were performed in air on a MOM Q-1500 D derivatograph. The heating rate was 10°C/min.

3. Results and discussion

The oxidative dehydrogenation of ethane over lanthana was reported before [6]. We discovered that lanthana exihibits a good reactivity for ethane, but the proportion of carbon dioxide is very high. This shows that lanthana is very selective for the complete oxidation of hydrocarbons. We prepared a lanthanum–calcium binary oxide catalyst. It is found that both ethane conversion and ethylene selectivity are improved over lanthanum–calcium oxide as compared to lanthana. It is noticed that the lanthanum–calcium oxide catalyst can be operated under our operation conditions with no decrease of activity for the ODH of ethane. Thus, this type catalyst is worthy of further improvement. The behaviour of lanthanum–calcium oxide catalysts with different lanthanum / calcium ratio in the ODH of ethane was firstly investigated. The results are listed in table 1. The data of lanthana are also included for comparison.

On lanthanum–calcium binary oxides higher ethane conversion and ethylene selectivity occur than on lanthana. The increase in ethane conversion and ethylene selectivity changes regularly according to the lanthanum / calcium atom ratio. The optimum of the lanthanum / calcium ratio is achieved at the value of 0.4. Lanthanum–calcium oxide at a La / Ca ratio of 0.4 is chosen for further investigation of the effect of addition of alkali metals. For each alkali-doped lanthanum–calcium oxide, the proportion of alkali metal is about 20 mol% of the total composition of the catalyst.

The activity data at 600°C for La / CaO and IA-doped La / CaO catalysts are shown in table 2. Ethane conversion and ethylene selectivity are further illustrated in fig. 1. The results of ODH of ethane show that moderate ethane conversion and ethylene selectivity can be achieved over a La/CaO catalyst. For Li-doped La/ CaO catalyst, the ethane conversion remains almost unaltered, but the ethylene selectivity increases remarkably. In the case of the Na / La / CaO catalyst, the behav-

Table 2
The performances of IA-doped La/CaO catalysts for oxidative dehydrogenation of ethane at 600°C (alkali metal/lanthanum/calcium = 1/1/2.5)

Catalyst	Conversion of C_2H_6 (%)	Product selectivity (%)				Yield of C_2H_4 (%)
		CO	CO_2	CH_4	C_2H_4	
La / CaO	48.8	0	25.0	0	75.0	36.6
Li / La / CaO	47.4	0	6.2	0	93.8	44.5
Na / La / CaO	48.9	0	19.5	0	80.5	39.4
K / La / CaO	23.3	0	7.1	0	92.9	21.6

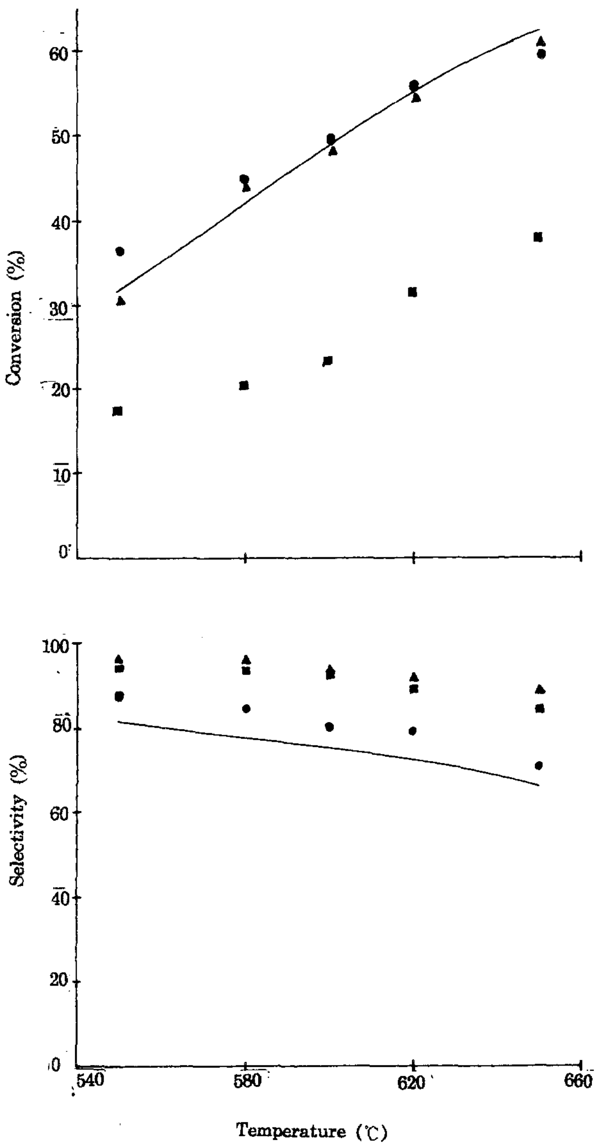

Fig. 1. Ethane conversion and ethylene selectivity with IA-doped La/CaO catalysts as a function of temperature (alkali metal/lanthanum/calcium = 1/1/2.5). (▲) Li/La/CaO; (●) Na/La/CaO; (■) K/La/CaO and (———) La/CaO.

iour of the ODH of ethane is similar to that over the Li/La/CaO catalyst. However, the Na/La/CaO catalyst exhibits a smaller increment for ethylene selectivity than the Li/La/CaO catalyst. With the K/La/CaO catalyst, the addition of potassium to La/CaO gives a catalyst with lower ethane conversion but higher ethylene selectivity compared to the La/CaO catalyst.

From results of the ODH of ethane, it can be easily found that increase of catalytic activity was not observed over doped La/CaO catalysts as a result of addition of an IA component. It means that over this type of catalysts, the catalytic activity is not contributed to by dopants. The role of dopants in the reaction is to increase ethylene selectivity. It is obvious that the catalytic activity decreases greatly (by more than 20%) in the case of the K-doped La/CaO catalyst. Table 3 summarises the surface areas of these three alkali-doped catalysts together with that of the undoped La/CaO sample. Although not presented here, the data of surface areas for the undoped La/CaO catalyst have no differences between the used sample after 6 h of reaction and the sample pretreated at 600°C but prior to reaction. The area loss from 6.34 m^2/g of the fresh sample to 0.58 m^2/g of the used sample occurs during pretreatment. As stated in footnote b to table 3, a test with the K/La/CaO sample shows an area of 0.34 m^2/g after pretreatment and 0.32 m^2/g after 6 h of reaction. For Li-doped and Na-doped La/CaO catalysts, the surface areas remain almost unaltered before and after use. The Li- and Na-doped La/CaO samples together with the undoped La/CaO sample nearly have the same surface areas after pretreatment or reaction although they have very different surface areas – much higher for the undoped La/CaO sample – in the fresh state. The identical surface areas are probably related to no differences in activity. The surface area of the used potassium-containing La/CaO sample is much lower than that of the other three used samples. It is clear that the low activity of the potassium-containing sample is due to differences in surface area. The decrease in surface area results in the reduction of the active sites.

From the above catalyst characteristics, it is also noted that lithium is a better promoter for increasing the ethylene selectivity than sodium although both as dopants for La/CaO oxides hardly exert any effect on the increase of the catalytic activity. It is obvious that the active sites of reaction on the La/CaO catalyst are inhibited by potassium. Therefore, we can conclude that potassium is a poor dopant for La/CaO catalyst for the ODH process of ethane compared to lithium and sodium.

Fig. 2 records XRD patterns of undoped and alkali-doped La/CaO catalysts. The XRD spectrum shows that most of the crystal phases for these catalysts are identical, although some peaks of the crystal phases of alkali-doped La/CaO catalysts shift from those of the undoped La/CaO catalyst. This means that the principal active crystal phases on these catalysts are similar and the addition of alkali metal to La/CaO only causes small

Table 3
Surface area of catalysts (alkali metal/lanthanum/calcium = 1/1/2.5)

Catalyst	Surface area (m^2/g)	
	fresh (not pretreated)	used [a]
La/CaO	6.34	0.58
Li/La/CaO	0.51	0.52
Na/La/CaO	0.56	0.53
K/La/CaO	1.82	0.32 [b]

[a] Standard conditions after 6 h of reaction at 600°C.
[b] The surface area following pretreatment but prior to reaction was 0.34 m^2/g.

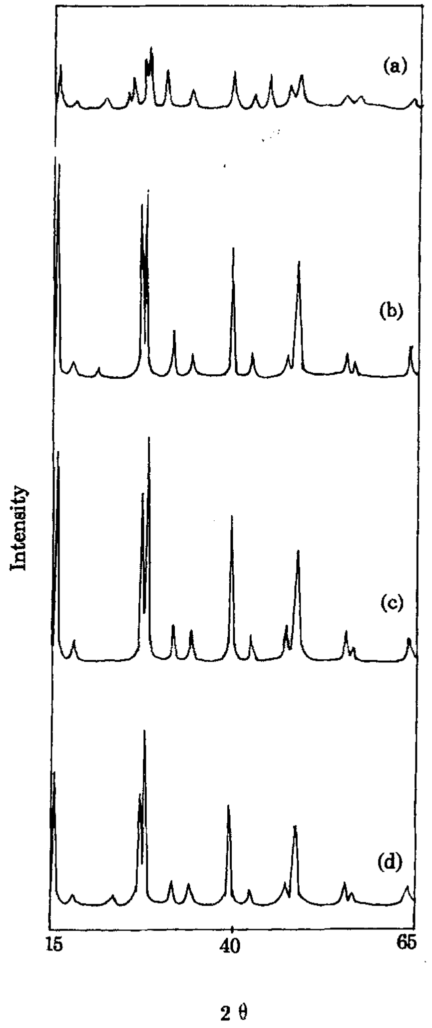

Fig. 2. XRD patterns for (a) La/CaO, (b) Li/La/CaO, (c) Na/La/CaO and (d) K/La/CaO (alkali metal/lanthanum/calcium = 1/1/2.5).

changes in the crystal phases of the La/CaO sample. Meanwhile, it can be seen that the XRD peak signals of alkali-doped La/CaO catalysts are much sharper than those of the undoped La/CaO catalyst. It is demonstrated that alkali-doped La/CaO catalysts have a better crystal structure than the undoped La/CaO sample. In addition, the relative intensities of peak signals of the undoped La/CaO sample changed after the alkali dopants were added. It reveals that one of the roles of dopants in the La/CaO catalyst is to promote the formation of a good crystal structure. There is no doubt that the high ethylene selectivity for the ODH of ethane over alkali metal doped La/CaO catalysts is closely connected to the good crystal structure, whereas the catalytic activity is not related to the crystal structure. As mentioned above, the surface areas of the samples are responsible for catalytic activity.

The results of thermogravimetry (TG) and differential thermogravimetry (DTG) for various La/CaO complex oxides are shown in figs. 3 and 4 respectively. It is found that a sharp weight loss and small changes of

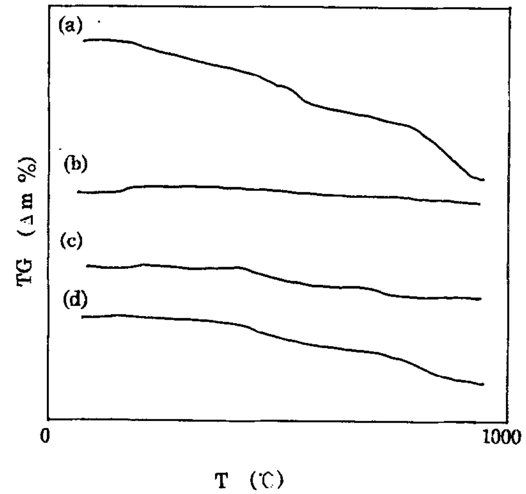

Fig. 3. TG curves for (a) La/CaO, (b) Li/La/CaO, (c) Na/La/CaO and (d) K/La/CaO (alkali metal/lanthanum/calcium = 1/1/2.5).

phases occur in the La/CaO catalyst in our investigated range of temperature. These phenomena can be explained from two aspects: one is that the process of phase changes results in the loss of some components in the catalysts and the other is that the phase changes are due to the loss of some thermal sensitive components in the catalysts. For lithium and sodium doped La/CaO catalysts, although there were changes of phases, small weight losses were observed. This means that the phase changes occur from one state to another state without altering the total chemical compositions of the complex oxides. In the case of the K/La/CaO catalyst, both weight loss and changes of phases were observed. However, the degree of weight loss is smaller than that of the binary La/CaO catalyst.

The results of TG and DTG show that the thermal stability of the chemical structure of the La/CaO binary

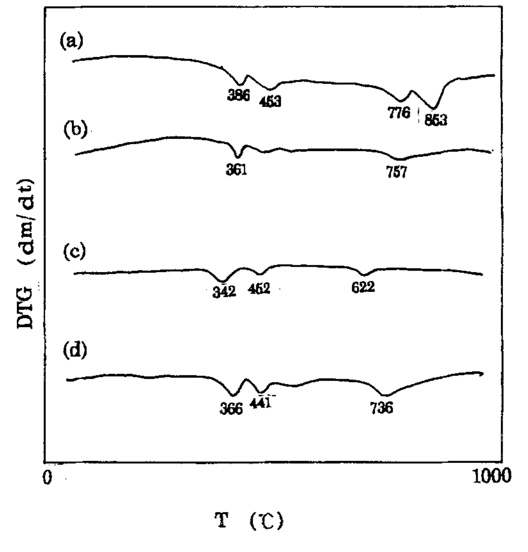

Fig. 4. DTG curves for (a) La/CaO, (b) Li/La/CaO, (c) Na/La/CaO and (d) K/La/CaO (alkali metal/lanthanum/calcium = 1/1/2.5).

oxide can be enhanced by the addition of alkali metals. The enhancement of thermal stability of the chemical structure probably contributes to the formation of a good crystal structure and the crystal structure is favorable for the increase of ethylene selectivity. For alkali metals, their respective addition to La/CaO promotes the thermal stability of the chemical structure, according to the change, in the order Li>Na>K. Lithium is the best dopant among the alkali metals for the thermal stability of the La/CaO chemical structure, which is related to the good ethane conversion and ethylene selectivity. For the K/La/CaO catalyst, the thermal stability of the chemical structure is weaker than that of both Li/La/CaO and Na/La/CaO catalysts. We suppose that low catalytic activity for the ODH of ethane over K/La/CaO catalyst more or less is connected to the weak thermal stability for which the loss of some active components is easy.

The results of product analysis (as shown in tables 1 and 2) reveal that no methane was detected in the products in the process of ODH of ethane over this class of catalysts. The main side reaction was combustion of hydrocarbons. Probably the combustion products are produced in a route parallel to that giving rise to the formation of ethylene.

The addition of lithium to the La/CaO catalyst results in an obvious increment of ethylene selectivity. Thus, further study of the Li/La/CaO catalyst is needed. The effect of the content of lithium in Li-doped La/CaO catalyst on catalytic activity and ethylene selectivity was investigated to correlate superior reactivity with the role of lithium. The relation between lithium content and reactivity at 600°C is plotted in fig. 5.

The results of various Li-doped La/CaO catalysts demonstrate that at low Li/La ratio (≤ 1), ethane conversion remains almost constant compared to the lithium-free La/CaO catalyst. However, at high Li/La ratios (> 1), the ethane conversion decreases. In contrast to the case of undoped La/CaO oxide, the ethylene selectivity increases over all Li-doped La/CaO catalysts, but the maximum increase in ethylene selectivity is attained at a Li/La ratio of 1.

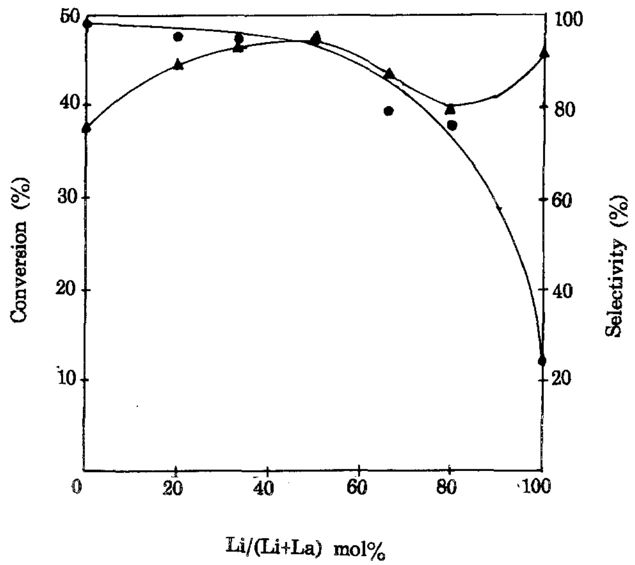

Fig. 5. Ethane conversion and ethylene selectivity at 600°C with Li-doped La/CaO catalysts as a function of composition at 1/2.5 of lanthanum/calcium. (●) Ethane conversion; (▲) ethylene selectivity.

It is noted that ethylene selectivity over Li-doped La/CaO catalysts is influenced by the lithium component. Activity data for Li/CaO catalyst presented in fig. 5 for comparison show that the ODH of ethane occurs over Li-doped CaO catalyst, which exhibits low activity and very high selectivity to ethylene. It seems that lithium is a superior dopant for this class of catalysts for increasing the ethylene selectivity. This can explain why the catalytic activity remains unaltered at low Li/La ratios. As for the decrease of catalytic activity at high Li/La ratios, it is possibly due to the suppression of active sites existing on the La/CaO catalyst by addition of too much lithium. The promotion of lithium for ethylene selectivity has been observed over each Li-doped La/CaO catalyst. However, the decrease of ethylene selectivity with the increase of Li/La ratio from 1 to 4 is somewhat confusing. We suppose that the component lithium play an important role in the increase of ethylene selectivity, but the increase of ethylene selectivity mostly comes from the contribution of coordinative action between lithium and lanthanum. A strong coordinative action between lithium and lanthanum exists at appropriate Li/La ratio (= 1). The action is getting weak with the gradual increase or decrease of lithium/lanthanum ratio from 1. For Li/La/CaO catalysts with high Li/La ratios, the weak coordinative action is probably related to the inhibition of active sites.

The behaviour of sodium-doped La/CaO catalyst in the ODH of ethane is similar to that of lithium-doped La/CaO catalyst (as shown in table 2 and fig. 1). The increment of ethylene selectivity is smaller over sodium-doped La/CaO catalyst than over lithium-doped La/CaO catalyst. We surmise that the function of sodium is mainly the promotion of ethylene selectivity by means of coordinative action between sodium and lanthanum, while the action is slightly weaker than that between lithium and lanthanum. Potassium as a dopant of La/CaO is especially notable for scavenging the active sites.

It was reported [11] that the formation of ethyl radicals is crucial for oxidative dehydrogenation of ethane. The present results show that probably the activation of ethane is carried out over lanthanum–calcium complex oxides to produce ethylene radicals which is responsible for the further reaction.

4. Conclusions

La/CaO is a very effective catalyst for the oxidative dehydrogenation of ethane. Ethylene selectivity over the catalyst increases by addition of alkali metals. The crystal structure of La/CaO oxide is also improved by adding alkali metals. For lithium- and sodium-doped La/CaO catalysts, the promotion of ethylene selectivity is mainly due to the coordinative action between the components lithium and lanthanum or sodium and lanthanum. The coordinative action of components in Li/La/CaO is stronger than that in the Na/La/CaO catalyst. Probably, the good thermal stability of the chemical structure for Li/La/CaO is favorable for the strong coordinative action of components which results in high ethylene selectivity. Although the addition of potassium to La/CaO promotes the increment of ethylene selectivity, the promotion is strongly counteracted by the decrease of catalytic activity. Therefore, unlike lithium and sodium, potassium is a poor dopant of La/CaO catalyst for the ODH reaction of ethane.

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