Excellent promotion by lithium of a lanthanum–calcium oxide catalyst for oxidative dehydrogenation of ethane to ethene

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New effective lanthanum–calcium oxides doped with alkali metals are highly selective for oxidative dehydrogenation of ethane to ethene; > 90% of ethene selectivity with > 40% ethene yield is attained over Li-doped La/CaO catalyst at 580–620 °C.

Much attention has been paid to the conversion of light alkanes to alkenes. The catalytic oxidative dehydrogenation of ethane to ethene has become important in the last decade and a variety of solids have been examined as catalysts for the oxidative dehydrogenation of ethane. Research upon Li/MgO[1–3] and V–Mo[4,5] oxide catalysts have been extensive. We have studied lithium–bismuth–calcium oxide[6] which shows good activity and excellent selectivity for ethene. This research is mainly focused on the search for more effective catalysts and this paper reports a new class of lanthanum–calcium oxide catalyst promoted by alkali metals for oxidative dehydrogenation of ethane. This new class of oxide catalysts exhibits high catalytic activity and excellent ethene selectivity, which opens a promising field of catalyst investigation.

The La/CaO catalyst was prepared by a precipitation method: powdered calcium hydroxide was added to lanthanum nitrate solution and the co-precipitate which formed was filtered off and dried overnight at 120 °C. La/CaO catalysts doped with alkali metals were prepared by wet mixing, the wet La/CaO precipitate being mixed with an alkali-metal nitrate solution. Each wet mixture was stirred and heated to evaporate the water until a thick paste was obtained which was then dried overnight at 120 °C. The dried samples were calcined in air at 600 °C for 10 h and the atomic ratio of alkali metal : lanthanum : calcium in the products was 1 : 1 : 2.5. The catalysts were tested for oxidative dehydrogenation of ethane using a fixed-bed continuous flow microreactor. The feed consisted of 15% ethane, 8.5% oxygen and 76.5% nitrogen. The reactants and products were analysed by a gas chromatograph equipped with a Porapak Q column for C_2H_6, C_2H_4, CO_2 and a 5 Å sieve column for CO, CO_2 and CH_4. The carbon mass balances in the reactions were generally > 95%.

Table 1 The performances of undoped and alkali-metal doped La/CaO catalysts for oxidative dehydrogenation of ethane

Catalyst	Conversion (%) C_2H_6	Product selectivity (%) CO	CO_2	CH_4	C_2H_4	Yield (%) C_2H_4
La/CaO	48.8	0	24.8	0.2	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

Table 2 The performances of ethane on the Li/La/CaO catalyst as a function of reaction temperature at GHSV = 1000 h^{-1}

Reaction temperature /°C	Conversion (%) C_2H_6	Product selectivity (%) CO	CO_2	CH_4	C_2H_4	Yield (%) C_2H_4
500	19.8	0	9.8	0	90.2	17.9
520	23.4	0	6.3	0	93.7	21.9
550	30.8	0	4.2	0	95.8	29.5
580	42.6	0	4.8	0	95.2	40.6
600	47.4	0	6.2	0	93.8	44.5
620	54.0	0	10.8	0	89.2	48.2
650	60.4	0	24.8	0	75.2	45.4

Table 1 shows the activity data for La/CaO and alkali-metal doped La/CaO catalysts. The reaction was conducted at 600 °C with a gas hourly space velocity (GHSV) of 1000 h^{-1}. It can be seen that 48.8% ethane conversion and 75.0% ethene selectivity are achieved over the La/CaO catalyst. For Li- and Na-doped La/CaO catalysts, the ethane conversion is almost unaltered, but selectivity towards ethene improves remarkably; 93.8% of selectivity towards ethene is attained over the Li-doped La/CaO catalyst, nearly 20% higher than over undoped La/CaO. It is clear that promotion by Li is greater than that of Na for ethene selectivity. With the K/La/CaO catalyst, the addition of potassium to La/CaO gives a catalyst which gives only 23.3% ethane conversion but 92.9% ethene selectivity compared to undoped La/CaO; overall, the addition of K to La/CaO results in lower ethlene yield.

Table 2 further illustrates the performances of ethane on lithium-doped La/CaO catalyst as a function of reaction temperature. It is noted that ethane conversion increases substantially with increase of reaction temperature and 60.4% conversion is achieved at 650 °C. Selectivity towards ethene reaches a maximum of 95.8% at 550 °C and gradually decreases above the temperature. In the range 500–620 °C, ethene selectivity is > 90%. It is evident that Li/La/CaO catalyst is highly selective toward formation of ethene over a wide temperature range. On the other hand, the yield of ethene reaches a maximum of 48.2% at 620 °C. By studying the dependence of reactivity and ethene selectivity over Li-doped La/CaO catalyst with reaction temperature, it is concluded that lithium exhibits most favourable promotion in the temperature range 580–620 °C for oxidative dehydrogenation of ethane.

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Received, 22nd January 1996; Com. 6/00466K