Calcium–Nickel–Lithium Oxide: a High Selectivity Catalyst for the Oxidative Dehydrogenation of Ethane to Ethylene

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Novel calcium–nickel oxides promoted by alkali metal are shown to be highly selective for the oxidative dehydrogenation of ethane to ethylene; 93.6% selectivity for ethylene with 25% ethane conversion over $Ca_1Ni_{0.4}Li_{0.35}$ oxide catalyst is attained at 600 °C.

Conversion of light hydrocarbons has received much attention. The oxidative dehydrogenation of ethane has been extensively studied over several oxide catalyst systems such as Mo–V–Nb,[1,2] MnAPO-5[3] and Li/MgO.[4–6] Current research focuses mainly on the search for more effective catalysts, especially with high selectivity for ethylene and good stability for selective oxidation of ethane. The present paper reports the oxidative dehydrogenation of ethane to ethylene over a new class of calcium–nickel oxides promoted by different alkali metal ions; the calcium–nickel–lithium oxide catalyst exhibits 93.6% selectivity for ethylene at 600 °C.

All catalysts examined in this work were prepared by wet impregnation method. $Ca(OH)_2$ was added to a mixed aqueous solution containing nickel nitrate and alkali metal nitrate. The solution was evaporated until a thick paste was formed. The mixture was dried at 120 °C overnight and calcined at 600 °C for 8 h. The oxidative dehydrogenation of ethane was carried out in a flow fixed-bed reactor loaded with about 1 g catalyst. The mixture of reactants contained 10% ethane, 8% oxygen, and nitrogen (82%). Reactants and products were analysed by on-line gas chromatography, using a Porapak Q column for C_2H_6, C_2H_4, CO_2 and a 5 Å molecular sieve column for CO, CO_2 and CH_4.

Table 1 shows the reaction performances of the oxidative dehydrogenation of ethane over a series of alkali metal promoted calcium–nickel oxide catalysts. The reaction was performed at 600 °C and ethane gas hourly space velocity (GHSV) = 1640 h^{-1}. It is very interesting to note that both $Ca_1Ni_{0.4}$ and $Ca_1Ni_{0.6}$ were completely non-selective for the formation of ethylene at 600 °C. In fact, they were much more selective for the formation of CO, a selectivity of 97.2 and 83.8% could be achieved on $Ca_1Ni_{0.4}$ and $Ca_1Ni_{0.6}$, respectively. However, the addition of alkali metal to calcium–nickel oxides remarkably improved the selectivity for ethylene, especially in the case of $Ca_1Ni_{0.4}Li_{0.35}$, a 93.6% of selectivity for ethylene with nearly 25% of ethane conversion was attained at 600 °C. The other $Ca_1Ni_{0.6}Li_{0.35}$ oxide catalyst, although its conversion was relatively low, also exhibited 93.5% of selectivity for ethylene. It seems that the selectivity

Table 1 The reaction performance of oxidation of ethane at 600 °C on a variety of alkali-promoted calcium–nickel oxide catalysts

Catalyst	C_2H_6 conversion (%)	Product selectivity (%)				Yield of C_2H_4 (%)
		C_2H_4	CH_4	CO	CO_2	
$Ca_1Ni_{0.4}K_{0.37}$	31.2	12.8	76.3	0.0	10.9	4.0
$Ca_1Ni_{0.6}K_{0.35}$	20.4	22.5	72.5	0.0	4.9	4.6
$Ca_1Ni_{0.4}Na_{0.35}$	24.7	37.7	59.5	0.0	2.8	9.3
$Ca_1Ni_{0.6}Na_{0.35}$	12.1	81.0	8.3	0.0	10.7	9.8
$Ca_1Ni_{0.4}Li_{0.35}$	24.9	93.6	0.0	2.4	4.0	23.3
$Ca_1Ni_{0.6}Li_{0.35}$	15.4	93.5	0.0	0.0	6.5	14.4
$Ca_1Ni_{0.4}$	42.3	0.0	2.1	97.2	0.7	0.0
$Ca_1Ni_{0.6}$	80.1	0.0	12.7	83.8	4.0	0.0

Table 2 The variation of the oxidation reaction performances of ethane on $Ca_1Ni_{0.4}Li_{0.35}$ catalyst as a function of reaction temperature, ethane GHSV = 1640 h^{-1}

Reaction temperature (°C)	C_2H_6 conversion (%)	Product selectivity (%)				Yield of C_2H_4 (%)
		C_2H_4	CH_4	CO	CO_2	
520	6.4	92.2	0.0	6.3	1.6	5.9
550	12.1	94.5	0.0	3.8	1.7	11.4
580	18.2	94.0	0.0	3.3	2.7	17.1
600	24.9	93.6	0.0	2.4	4.0	23.3
620	32.5	89.2	0.9	1.5	8.3	29.0
650	40.8	86.8	0.7	1.5	11.0	35.4

for ethylene on alkali metal promoted calcium–nickel oxide catalysts decreased in the order of Li > Na > K. It is also interesting that the conversion of ethane on the calcium–nickel oxides increased with increasing the amount of nickel. On the contrary, the conversion of ethane on the alkali metal doped calcium–nickel oxide catalysts decreased with an increase in the amount of nickel.

Table 2 illustrates the variation of the oxidation reaction performances of ethane on the $Ca_1Ni_{0.4}Li_{0.35}$ catalyst as a function of reaction temperature. It can be seen that the conversion of ethane increased substantially with increasing reaction temperature, whereas the selectivity for ethylene, after reaching a maximum of 94.5% at 550 °C, slightly decreased. A 40.8% of ethane conversion and 86.8% of selectivity for ethylene could be achieved at 650 °C.

The activity of the catalyst might be improved further. It is clear that the distinctive behaviour of the doped and undoped catalyst is worth further investigation.

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References

1 E. M. Tharsteinson, T. P. Wilson, F. G. Young and P. H. Kasai, *J. Catal.*, 1978, **52**, 116.
2 R. Burch and R. Swarnakar, *Appl. Catal.*, 1991, **70**, 129.
3 B. Z. Wan and K. Huang, *Appl. Catal.*, 1991, **73**, 113.
4 E. Morales and J. H. Lunsford, *J. Catal.*, 1989, **118**, 255.
5 S. T. Conway and J. H. Lunsford, *J. Catal.*, 1991, **131**, 513.
6 H. M. Swaan, A. Toebes, K. Seshan, J. G. Van Ommen and J. R. H. Ross, *Catal. Today*, 1992, **13**, 629.