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Comparison of behaviour of rare earth containing catalysts in the oxidative dehydrogenation of ethane

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Abstract

Catalyst promotion by addition of either La and Sm to MgO or Na aluminate to Sm_2O_3 and La_2O_3 has been investigated for the oxidative dehydrogenation of ethane in the temperature range 550–700°C. With all unpromoted and promoted catalysts, the selectivity to ethylene is strongly enhanced by the temperature, the highest values being obtained at 700°C. Sm_2O_3 is the most active among the bulk oxides, while samarium addition to MgO results in higher surface area, but does not enhance the catalytic activity. Ethylene productivity on La_2O_3 promoted MgO samples is higher than with pure La_2O_3, Sm_2O_3 and MgO, not only due to the stabilising effect of La on MgO surface area, but also due to a higher intrinsic activity. With both bulk oxides and rare earth promoted MgO, the selectivity to ethylene strongly increases by decreasing the O_2/C_2H_6 feed ratio, while it is quite unaffected by ethane conversion and catalyst composition, in agreement with the hypothesis that the main role of catalyst in the experimental conditions investigated is to produce ethyl radicals which are converted in the gas phase to CO and C_2H_4. When La_2O_3 is modified by the addition of sodium aluminate the catalytic behaviour significantly changes, likely due to a different, mostly heterogeneous reaction mechanism. On aluminate promoted lanthana, ethane is converted to ethylene with higher yields which do not depend on the feed ratio. Moreover, only CO_2 is produced as by-product, the formation of CO being quite negligible. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Rare earth catalysts; Oxidative dehydrogenation; Ethane

1. Introduction

A large number of catalysts have been proposed for the oxidative dehydrogenation (ODH) of ethane [1]. Bulk and supported transition metal oxides, working at 400–500°C through a redox cycle, give high selectivity to ethylene only at low ethane conversion [1], while rare earth metal oxides are active at higher temperature [2–7]. In particular, good performances have been obtained with La_2O_3 [2,7] and Sm_2O_3 [2,4,5], whereas CeO_2 and Pr_6O_{11} exhibit low selectivity to ethylene [2,3]. Moreover, it has been found that ethylene selectivity increases with increasing temperature in the range 550–800°C [2,5]. The same behaviour has been observed for Na promoted $Ce_2(CO_3)_3$ [3] and Li or Sn promoted MgO [6], the latter catalysts showing basicity characteristics similar to rare earth oxides.

Due to their basicity and thermal stability, rare earth oxides have also been studied in the oxidative coupling of methane (OCM), both as bulk oxides [2,9,11–13] or MgO promoters [11,12,14]. Substantial yields of

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ethylene are obtained only at high temperatures (up to 900°C), the reaction mechanism involving ethane ODH [3,8–10]. Better performances in terms of both selectivity and activity in OCM have been exhibited with Li/MgO, but this catalyst undergoes a progressive loss of Li at high temperature [1]. Addition of other alkali such as Na to Sm_2O_3 [15] or CeO_2 [2] results in better catalytic performance.

The nature of surface oxygen species involved in ethane ODH over rare earth oxides is still debated. The influence of O_2 partial pressure on the process selectivity has been investigated for ceria based catalysts [3].

In this paper, the catalytic properties in the ethane ODH of samarium and lanthanum promoted magnesia, and sodium aluminate promoted samarium and lanthanum oxides have been compared under different experimental conditions such as temperature, contact time and feeding ratio. Differences of catalytic behaviour of promoted and unpromoted catalysts are discussed.

2. Experimental

Lanthanum and samarium bulk oxides were obtained by thermal decomposition of $La(NO_3)_3{\cdot}6H_2O$ or $Sm(NO_3)_3{\cdot}6H_2O$ heating from 10 to 700°C in flowing air ($100\,cm^3\,min^{-1}$) for 3 h. Earth oxide promoted catalysts were prepared by wet impregnation of MgO with lanthanum or samarium nitrate aqueous solution. MgO samples were obtained by decomposition of $MgCO_3$ in flowing air at 600°C for 5 h. Promoted earth oxide catalysts were prepared by adding $NaAlO_2$ to rare earth nitrate aqueous solutions and evaporating water. All materials were dried at 120°C and calcined at 700°C in flowing air.

The list of catalysts is reported in Table 1. The catalysts are indicated as *x*Ln/Mg or *x*Ln-Na, where *x* is the rare earth oxide weight percentage and Ln indicates Sm or La oxide. The promoted MgO catalysts have a rare earth oxide nominal content of 5 and 10 wt.%, while the promoted earth oxide samples contain 10 wt.% of $NaAlO_2$.

XRD analysis was performed with a PW 1710 Philips diffractometer. The BET surface areas were measured by N_2 adsorption at 77 K with a Carlo Erba 1900 Sorptomatic.

The catalytic activity tests were carried out with the experimental apparatus described in [16] using a fixed bed quartz micro-reactor at atmospheric pressure. In order to limit the eventual homogeneous contributions to ethane conversion, α-Al_2O_3 pellets were loaded upside the catalytic bed and the reactor diameter was reduced in the post-catalytic zone. The contact time ranged from 2×10^{-3} to $350\times10^{-3}\,g\,s\,Ncm^{-3}$, the reaction temperature from 550 to 700°C. The C_2H_6 concentration was 4 vol.% and the feed ratio O_2/C_2H_6 ranged from 0.1 to 1. Carbon balances were close to ±2%.

3. Results and discussion

The XRD spectra of the bulk rare earth oxide samples show the presence of pure La_2O_3 or Sm_2O_3 phases; signals of $La(OH)_3$ have also been detected in the XRD spectrum of lanthanum oxide due to the strong tendency to hydration of this oxide. Sharper XRD peaks are shown by Sm_2O_3 with respect to La_2O_3, indicating higher crystallisation of the former oxide, also confirmed by the lower value of the surface area (Table 1). XRD spectra of La/Mg and Sm/Mg catalysts show the signals of MgO in addition to very weak signals of La_2O_3 for both La-containing samples and of Sm_2O_3 for the sample 10Sm/Mg. The initial surface area of MgO ($84\,m^2\,g^{-1}$) is dramatically reduced upon treatment at 700°C ($18\,m^2\,g^{-1}$), while it is partially preserved by the presence of the rare earth oxide, as also found by Choudhary et al. [11]. The main signals of $La(OH)_3$ and Sm_2O_3 were also found in the XRD spectra of 90La-Na and 90Sm-Na samples, respectively, together with peaks of rare earth aluminate.

Reaction tests carried out at 700°C in the absence of catalyst have indicated that the contribution of homogeneous reactions to the conversion of ethane is negligible under the experimental conditions investigated by us. In all the catalytic runs, the only reaction products detected were C_2H_4, CO and CO_2. No deactivation effects were observed in 12 h runs.

Fig. 1 reports the ethane conversion and the selectivity to reaction products against (1a) temperature and (1b) contact time *W*/*F* (*W* is the catalyst weight, *F* the total volumetric gas flow rate at standard con-

Table 1
Surface area, ethylene productivity, rate of ethane consumption and selectivity to ethylene evaluated at 700°C. Feed: C_2H_6 (4 vol.%), O_2 (2 vol.%), balance He

Catalysts	Surface area ($m^2\ g^{-1}$)[a]	Ethylene productivity ($kg\ kg^{-1}\ h^{-1}$)	$r_{C_2H_6} \times 10^6$ ($mol\ s^{-1}\ m^{-2}$)[b]	Ethylene selectivity
MgO	18	1.7	1.5	0.62
La_2O_3	34	1.2	0.61	0.57
Sm_2O_3	5	4.0	14.3	0.55
5La/Mg	40	5.6	2.6	0.53
10La/Mg	35	3.6	2.0	0.51
5Sm/Mg	28	1.4	0.98	0.49
10Sm/Mg	58	2.7	0.89	0.53
90La-Na	9	1.2	1.5	0.79
90Sm-Na	3	0.70	3.9	0.58

[a] After catalyst calcination at 700°C.

[b] Rate of ethane consumption calculated in conditions of differential reactor.

ditions) for bulk Sm_2O_3, chosen as representative of the behaviour of pure oxide catalysts.

An increase of selectivity to ethylene and a decrease of selectivity to carbon oxides are observed by increasing the temperature (Fig. 1a). More specifically, CO_2 is the main product of ethane oxidation at low temperature, while with increasing temperature not only C_2H_4 become predominant, but also a different distribution between CO_x is observed, the selectivity to CO decreasing much more slightly compared to that of CO_2. On the other hand, product selectivities are very weakly affected by the contact time (Fig. 1b), when compared to the effect of the reaction temperature. Indeed, in the same range of ethane conversion, the selectivity to ethylene changes from 20 up to about 60% with temperature and from 60 to 54% with contact time. A similar behaviour was found by Kennedy and Cant [3] for Na promoted $Ce_2(CO_3)_3$ catalysts.

According to the assumptions of Morales and Lunsford [17] on the reaction mechanism, the observed effect of temperature on ethane ODH could be attributed to the favoured release of ethyl radicals from the catalyst surface at higher temperatures, resulting in a reduced production of surface ethoxy species responsible for the formation of gaseous CO_2. The weak dependence of the selectivity to ethylene on contact time, which is something unusual in oxidehydrogenation or, more generally, in partial oxidation reactions, would be explained by the occurrence of parallel reaction paths producing ethylene and CO in the gas phase according to radical mechanisms, starting from ethyl radicals generated with high formation rate on the catalyst surface.

A negative effect of temperature on C_2H_4 selectivity in ethane ODH has also been observed, but in very different experimental conditions, by Buyevskaya

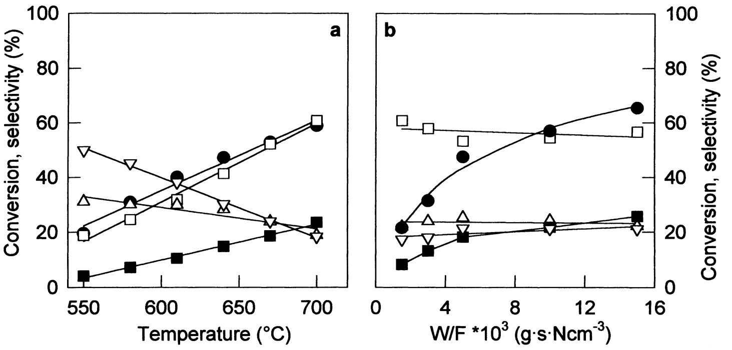

Fig. 1. O_2 (●) and C_2H_6 (■) conversion and selectivity to C_2H_4 (□), CO (△), and CO_2 (▽) as functions of the (a) temperature (with $W/F=0.004\ g\ s\ Ncm^{-3}$), and (b) contact time (with $T=700°C$) for Sm_2O_3. Feed: C_2H_6 (4 vol.%), O_2 (2 vol.%), balance He.

et al. [12] with a TAP reactor by pulsing C_2H_6 on Sm_2O_3 in the absence of gaseous O_2, and by Ji et al. [7] for a La/CaO catalyst at high reactant concentrations (C_2H_6=15.2 vol.%, O_2=8.6 vol.%).

Table 1 reports the activity data of all catalysts at 700°C, since for all of them, the effect of increasing temperature is to increase the selectivity to ethylene. The values of ethylene productivity and ethane consumption per unit surface area have been evaluated under differential reactor conditions. With reference to the bulk oxides, it can be seen that La_2O_3 is less active than Sm_2O_3, in agreement with Burch and Tsang [5], while MgO shows intermediate activity. Although bulk Sm_2O_3 is more active than La_2O_3, the activity of Sm/Mg is lower than that of La/Mg for both samples. The main effect of rare earth oxide addition to MgO is likely to stabilise the catalyst surface area and consequently to increase the overall activity per unit mass, although some marked differences should be pointed out between La and Sm promoted samples. In particular, the addition of La_2O_3 to MgO enhances the productivity of ethylene (Table 1, column 3), although not monotonically, the most active sample being 5La/Mg. The surface area of the samples depends in the same way on lanthanum content. Nevertheless, the activity per unit surface area of 5La/Mg and 10La/Mg is higher compared to both Mg and La pure oxides, indicating the occurrence of an effective promoting action of lanthanum. On the contrary, even if the surface area of both Sm/Mg samples is higher than that of pure MgO, their activity per unit area is slightly lower.

A similar effect of lanthanum content in La/MgO catalysts was found by Choudhary et al. [11] in the case of methane oxidative coupling reaction. They found a non-monotonical increase of surface area with increasing La content and a higher activity in comparison to pure MgO.

In Table 1, the ethylene selectivity, evaluated at very low ethane conversion, when the eventual further oxidation of C_2H_4 to CO_x is negligible, is also reported. It appears that the selectivity values of both bulk oxides and promoted MgO catalysts are not significantly affected by the catalyst composition. This lack of dependence could be related to the occurrence of a hetero–homogeneous process, by which the products distribution should be controlled by gas phase radical reactions, the role of catalyst being mostly that of producing ethyl radicals faster than by thermal cracking.

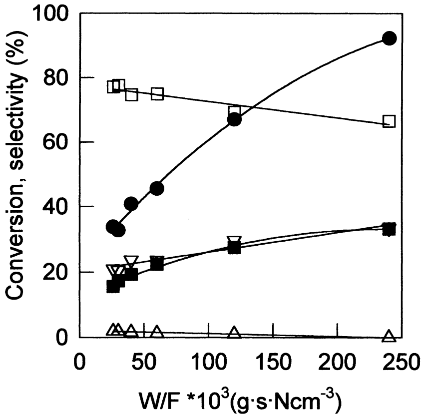

Fig. 2. O_2 (●) and C_2H_6 (■) conversion and selectivity to C_2H_4 (□), CO (△), and CO_2 (▽) as a function of the contact time for 90La-Na at 700°C. Feed: C_2H_6 (4 vol.%), O_2 (2 vol.%), balance He.

Although these catalysts do not show very high selectivities under the experimental conditions investigated, many of them give high ethylene productivity (Table 1) in comparison to that achieved with other catalysts reported in [1], reaching the best value with 5La/Mg (5.6 kg of ethylene per kg of catalyst and per hour).

A markedly higher value of ethylene selectivity (79%) is shown by 90La-Na with respect to the other catalysts (Table 1). In Fig. 2, the effect of the contact time on the products selectivity at 700°C is reported, showing that the initial ethylene selectivity decreases by increasing the contact time, indicating a non-negligible effect of C_2H_4 oxidation consecutive step. This behaviour is more similar to that exhibited by transition metal oxides catalysts, operating in a lower temperatures range through a heterogeneous reaction mechanism. Another characteristic of this catalyst is that the oxidation of ethane leads mostly to CO_2 by-production, only negligible amounts of CO being found with this catalyst in all the range of *W*/*F* values.

By taking into account that (i) a gas phase radical mechanism should produce ethylene with a given selectivity, the remaining C_2H_6 being converted to CO, (ii) it is well known that at 700°C the gas phase oxidation of CO to CO_2 proceeds at a very low reaction rate, and (iii) the catalysed oxidation of CO is usually much faster than the combustion of light alkanes, the

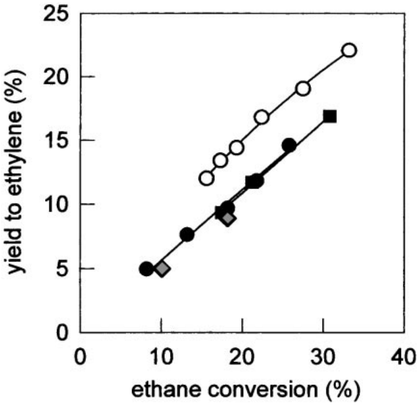

Fig. 3. C_2H_4 yield as a function of the C_2H_6 conversion over Sm_2O_3 (●), 5La/Mg (■), 5Sm/Mg (◆) and 90La-Na (○) at 700°C. Feed: C_2H_6 (4 vol.%), O_2 (2 vol.%), balance He.

results obtained with 90La-Na suggest that a heterogeneous formation of both products could be assumed. Hence, a different reaction mechanism should be hypothesised for this catalyst.

Some different results with respect to 90La-Na have been obtained with 90Sm-Na. In comparison with unpromoted samarium oxide, a negligible effect on selectivity to ethylene was found; however a strong, even if less marked than with 90La-Na, reduction of CO selectivity with respect to CO_2 selectivity was observed.

The different behaviour of 90La-Na catalyst is also evidenced by the data of Fig. 3, where the yield to C_2H_4 is reported as a function of the conversion of C_2H_6. It is seen that the yield values relevant to Sm_2O_3, 5La/Mg and 5Sm/Mg stay on a single curve and are typical of the homogeneous process operating under the same conditions, strongly supporting the assumption that the main role of these catalysts is to produce ethyl radicals. The ethylene yields increase with increasing ethane conversion as an effect of the unchanged ethylene selectivity with increasing contact time. A different curve has been found for 90La-Na which exhibit higher selectivity leading to higher ethylene yield. This confirms that the role of 90La-Na should be not only to simply produce ethyl radicals but also to activate a more complex mechanism over its surface.

The effect of feeding ratio $R=O_2/C_2H_6$ on the catalyst performances is shown in Fig. 4 for Sm_2O_3 and 90La-Na, chosen as representative of the two different catalytic behaviours. With both catalysts, the conversion of ethane increases and the selectivity to ethylene decreases by increasing the oxygen concentration. However, the decrease of C_2H_4 selectivity is very strong on Sm_2O_3, while a weaker dependence is observed for 90La-Na. This difference should be related to a different dependence of ethylene formation rate of oxygen partial pressure and then to a different mechanism involving adsorbed or lattice oxygen on the two catalysts. A similar behaviour was found by Kennedy and Cant [3] for Na-Ceria catalysts.

In order to better elucidate the effect of the O_2 partial pressure, the selectivity to ethylene is reported as a function of ethane conversion for both Sm_2O_3 and

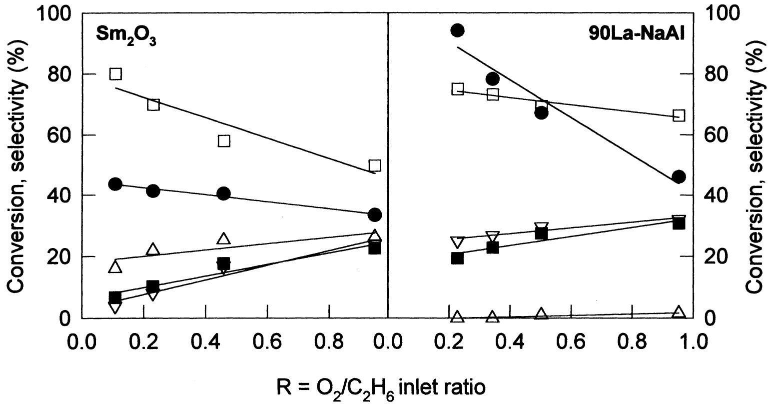

Fig. 4. O_2 (●) and C_2H_6 (■) conversion and selectivity to C_2H_4 (□), CO (△), and CO_2 (▽) as functions of O_2/C_2H_6 feeding ratio for Sm_2O_3. ($W/F=3\times10^{-3}$ g s N cm^{-3}) and 90La-Na ($W/F=120\times10^{-3}$ g s N cm^{-3}) at 700°C; C_2H_6 inlet concentration=4 vol.%.

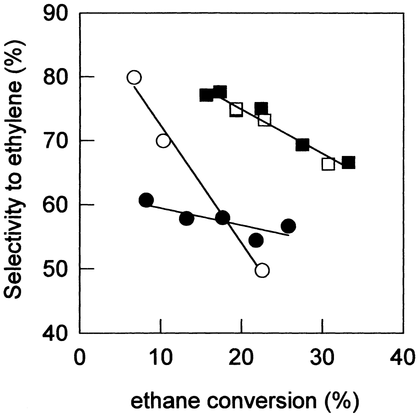

Fig. 5. C_2H_4 selectivity as a function of the C_2H_6 conversion over Sm_2O_3 (●, ○) and 90La-Na (■, □) at 700°C. Filled symbols: *W*/*F* variable (stoichiometric feed); open symbols: O_2/C_2H_6 feed ratio variable (at constant *W*/*F*).

90La-Na catalysts, for two sets of data, obtained with (i) increasing the contact time at constant feed ratio, or (ii) increasing the O_2/C_2H_6 feed ratio at constant contact time (Fig. 5). As shown by the superimposition of the two curves relevant to 90La-Na, in this case the selectivity to ethylene is not actually affected by the O_2 partial pressure, but it depends only on the ethane conversion, either if increasing with O_2 partial pressure or with the contact time. On the other hand, the catalytic behaviour of Sm_2O_3 is strongly influenced by the O_2 partial pressure since the two curves shown in Fig. 5 are markedly different. These results seem to confirm that the role played, respectively, by adsorbed and lattice oxygen in the ethane activation should be very different on Sm_2O_3 or 90La-Na. In agreement with previous findings of Choudhary et al. [14], who found that lattice oxygen is involved in the ethane selective oxidation on MgO supported La_2O_3 and Sm_2O_3, our results on Sm_2O_3 suggest that the selectivity to ethylene is strongly increased by lowering O_2 partial pressure, i.e. by decreasing the amount of adsorbed oxygen species.

The weak dependence of selectivity to ethylene on O_2 partial pressure for 90La-Na further supports our hypothesis of a mostly heterogeneous reaction mechanism. In fact, a strong effect of the feeding ratio is expected on reaction selectivity, if the catalyst acts only as radicals activator, since it is well known that selectivity to ethylene of a homogeneous process is more and more favoured under fuel-rich concentrations.

4. Conclusions

The catalytic properties of pure and mixed oxides based catalysts containing Sm, La and Mg have been investigated in ethane ODH. Sm_2O_3 is the most active catalyst among pure oxides, but addition of samarium oxide to MgO, still producing an increase of surface area, does not enhance the catalytic activity. La_2O_3 strongly increases the activity of MgO resulting in very high ethylene production rate, not only due to the stabilising effect of La on catalyst surface area, but also due to a higher intrinsic activity. Moreover, the selectivity to ethylene is strongly favoured at the highest values of temperature and C_2H_6/O_2 feed ratio investigated and poorly depends on ethane conversion and catalyst composition, except when La_2O_3 is promoted by the addition of sodium aluminate. This behaviour is in agreement with the assumption that the role of catalyst in the experimental conditions investigated is to produce ethyl radicals which react in the gas phase to produce CO and C_2H_4.

Significant differences have been found for Na promoted lanthana catalyst, for which a mostly heterogeneous reaction mechanism likely involving lattice oxygen, should be hypothesised, resulting in higher ethylene selectivity and by-production of only CO_2. With this catalyst, ethane is converted to ethylene with higher yields also with oxygen/ethane feeding ratio higher than the stoichiometric one.

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