

Catalytic Composites Based on Yttria Stabilized Zirconia for Oxidative Dehydrogenation of Ethane

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Abstract—LiCl/YSZ is found to be a very effective catalyst for the oxidative dehydrogenation of ethane. LiCl supported on YSZ-MgO composite shows increase in catalytic activity and ethylene selectivity. Addition of Mn and Sn as promoters to this system leads to 85% ethane conversion, 77% ethylene selectivity and 65% ethylene yield at 662 °C. Use of Li₂O in the place of LiCl results in lower ethylene yields. Further modification is needed to improve the catalyst stability.

Key words: Oxidative Dehydrogenation, Ethane, LiCl, YSZ, MgO, Catalyst Stability

INTRODUCTION

Ethylene, a most versatile building block material, is currently being produced by a highly energy-intensive process, involving thermal cracking of ethane/propane/naphtha/gas oil at temperatures above 800 °C. High investment costs, frequent shutdowns of the cracker units for de-coking, requirement of furnace tubes of special metallurgy and periodic replacement of the tubes are the other motivating factors behind the global research efforts to develop an economically viable alternative process for production of ethylene. Among the various alternative routes, catalytic oxidative dehydrogenation of ethane (ODE) to ethylene has received considerable attention, and the developments in this area have been covered by a number of exhaustive reviews [Cavani and Trifiro, 1995, 1999; Baerns and Buyevskaya, 1998; Banares, 1999]. Numerous catalyst formulations based on oxides of V-Nb-Mo, alkali (Li₂O) and alkaline earth oxides (MgO), rare earth oxides (of La, Nd, Sm & Dy) and their combinations with several transition metals oxides (Li-Mn-W/TiO₂ & Mn-Na₂WO₄/SiO₂) have been reported as effective catalysts for ODE [Liu et al., 1998].

LiCl supported on sulfated zirconia (SZ) has been found to be highly effective for ODE [Wang et al., 1999]. YSZ (yttria stabilized zirconia) is another support that is useful for ODE. Its ability to pump reactive oxygen through oxygen anion conduction is responsible for its activity in oxidative ethane dehydrogenation. Otsuka et al. [1995] reported that the role of YSZ was to increase the number of O* species responsible for the activation of ethane over B₂O₃/YSZ. Hamakawa et al. [1997] showed that ethane was partially oxidized to acetaldehyde by oxygen species generated electrochemically on an inert gold film via YSZ at 475 °C. Although YSZ does not possess solid super acid characteristics like SZ, yttria addition to zirconia makes the cubic structure of the zirconia stable and the oxygen vacancy, generated by the substitution of Zr⁴⁺ in the lattice by Y³⁺, functions as the active center for oxidative ethane dehydrogenation. In the present communication, attempts have been made

to enhance the oxidative dehydrogenation activity of YSZ by addition of LiCl as the active phase and further modifications with other active metals and supports like MgO.

EXPERIMENTAL

1. Catalyst Preparation

A commercial sample of YSZ (TZ8Y, 8 mole% yttria, M/s Tosho, Japan) was used as such a support for various YSZ-based catalyst systems. LiCl/YSZ was prepared by impregnation of LiCl (5 wt% as Li) on YSZ by incipient wetness method. The sample after drying at 120 °C for 6 h was subsequently calcined at 700 °C for 3 h.

LiCl/MgO sample was also prepared in a similar manner by impregnation of LiCl (5 wt% as Li) on commercial Mg(OH)₂ (BDH, 95%) powder, drying and calcination at 700 °C for 3 h.

A composite support consisting of 50% w/w mixture of YSZ and MgO was prepared by wet mixing of required quantities of Mg(OH)₂ and YSZ powders in water to get a thick slurry, which was evaporated to dry with continuous stirring, dried at 120 °C and calcined at 700 °C for 3 h. On this composite support, appropriate quantities of Mn(NO₃)₂ and LiCl were impregnated by incipient wetness method to get 4 wt% Mn and 5 wt% Li loading and subjected to the drying and calcination procedures as above. For the impregnation of Sn (9 wt%), required quantity of SnCl₂·9H₂O was dissolved in acetone and impregnated on dried Li-Mn/MgO-YSZ, dried again and calcined as per the procedure above.

2. Catalytic Performance

Oxidative dehydrogenation of ethane was studied on these catalysts in a fixed bed by using a quartz reactor tube (id=4 mm, total length=450 mm) in which the catalyst (0.3 to 1 g, mixed with quartz chips as diluents) was loaded in the middle of the tube in a bulb (id=8 mm, length=65 mm) fitted with sintered disc at the bottom to hold the catalyst. Quartz chips were filled above and below the bed to minimize gas phase reaction. Temperature of the catalyst bed was monitored with a thermocouple located at the bed inlet. The feed, consisting of 10% ethane, 10% oxygen, 80% nitrogen, was introduced into the reactor through a pre-calibrated mass flow controller at a total flow rate of 30 ml/min. Ethane conversion <2% was

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Table 1. Performance of LiCl/YSZ and LiCl/MgO-YSZ based catalysts for ODE

Catalyst	Temp. (°C)	C ₂ H ₆ conversion (%)	C ₂ H ₄ selectivity (%)	C ₂ H ₄ yield (%)
LiCl/YSZ	665	75	79	60
LiCl/MgO	665	62	87	54
LiCl/YSZ-MgO	665	80	79	63
Mn-LiCl/MO-YSZ	650	88	71	63
Sn-Mn-LiCl/MgO-YSZ	662	85	77	65

Catalyst; 0.5 g, Feed; 10% C₂H₆, 10% O₂, 80% N₂, Flowrate; 30 ml/min.

observed when the reaction was conducted with quartz chips only indicating negligible contribution from homogeneous reaction.

The reactants and products were analyzed by a gas chromatograph equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). Hydrocarbons were analyzed by FID using a Porapak Q column and CO, CO₂, O₂, N₂, H₂ were detected by TCD with a 5A molecular sieve column.

RESULTS AND DISCUSSION

In the present work, LiCl has been used as the active phase, which has been subsequently modified with promoters like Mn & Sn. Pure YSZ and YSZ modified by addition of MgO have been used as supports.

1. Effect of Supports

Results of evaluation of catalysts with different supports, YSZ, MgO and YSZ-MgO are given in Table 1. 5 wt% LiCl/YSZ at 665 °C displays ethane conversion, selectivity and ethylene yield of 75%, 79% and 60% respectively. Corresponding values for 5 wt% LiCl/ZrO₂-SO₄ with the same feed composition and GHSV, but at 650 °C are 53%, 90% and 48% [Wang et al., 1999]. Compared to SZ, YSZ as a support for LiCl shows higher activity, but less selectivity. While ODE on YSZ is expected to proceed via surface peroxide [Otsuka et al., 1995] on SZ, its super acid character is believed to be responsible for activation of ethane.

Wang et al. [2000] have reported results of ODE on LiCl (3.5 wt%) supported on Al₂O₃, SiO₂, TiO₂, ZrO₂ and SZ. At 600 °C with both LiCl/Al₂O₃ and LiCl/ZrO₂ ethylene yields are poor, around 26–27%. While LiCl/SiO₂ and LiCl/TiO₂ display high yields, 78.6% and 64.8% respectively, they are prone to fast deactivation within first 5 h. Similarly, LiCl, when supported on oxides like MgO [Wang et al., 1995], NiO [Wang et al., 1995] and ZnO [Otsuka et al., 1989] also displays good activity for ODE as well as oxidative coupling of methane (OCM), but again undergoes fast deactivation. Only LiCl/SZ shows stable ethylene yield of ~50% over a duration of 50 h. It is reported [Wang et al., 2000] that the activity for ODE on these catalysts is related to their acid-base and redox properties, with Cl⁻ ions contributing towards selectivity.

Fig. 1 shows the stability of LiCl/YSZ for initial 2 h at 642 °C and for further 4 h at 662 °C with ethylene yields of 60%. LiCl/YSZ displays better stability compared to LiCl supported on Al₂O₃, SiO₂, TiO₂, ZrO₂, MgO, NiO & ZnO and is comparable with LiCl/SZ. Besides the intrinsic activity of LiCl for ODE, anion vacancies in YSZ have contributed towards the good performance and stability of LiCl/YSZ. Anion vacancies in YSZ are reported to be the active centers for other reactions like CO oxidation on CuO/YSZ [Dow

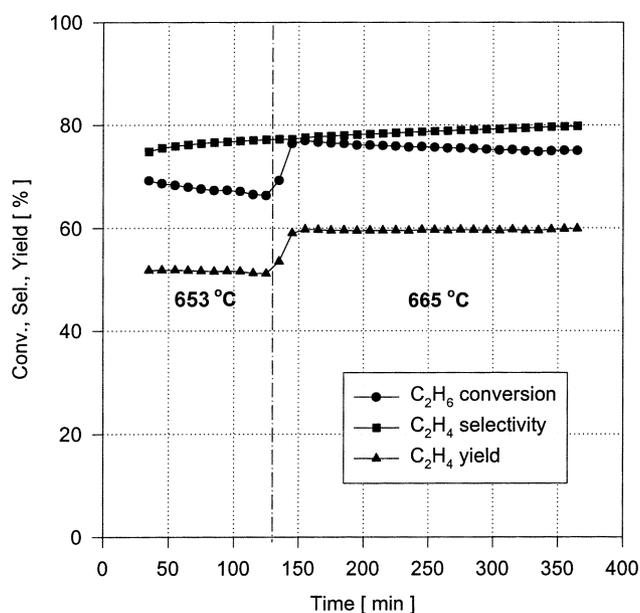


Fig. 1. Oxidative ethane dehydrogenation activity as a function of time on stream over LiCl/YSZ. Reaction conditions: 0.5 g catalyst, C₂H₆ : O₂ : N₂ = 1 : 1 : 8, flowrate=30 ml/min, T= 653–665 °C.

et al., 1996] and methanol synthesis on YSZ and Ca stabilized zirconia [Silver et al., 1989; Jackson and Ekerdt, 1990]. Xui-Mei et al. [1998] studied the oxidative coupling of methane by using the cell Ag-YSZ, 1 wt% Sr/La₂O₃-Ag-YSZ, and 1 wt% Sr/La₂O₃-Bi₂O₃-Ag-YSZ. YSZ acts as an oxygen ion conducting solid electrolyte and is widespread applied to fuel cells, oxygen pumps, and oxygen sensors. A number of oxide systems with anion vacancies, like SrFeO_{3-δ}Cl_δ [Dai et al., 1999], are known to be effective catalysts for ODE.

On a basic support like MgO, LiCl displays lower conversion (62%) but higher selectivity (87%) under identical reaction conditions. On similar Li⁺-MgO-Cl⁻ systems studied earlier [Wang et al., 1995], 75% ethane conversion and 77% ethylene selectivity at 620 °C have been observed. Ethylene yields are comparable in both cases (54 & 55% respectively), but GHSV in the present case is higher, (0.5 g and 30 ml/min compared to 5.2 g and 60 ml/min in earlier work) indicating higher intrinsic activity, although the reaction temperature is higher by 30 °C, with nearly same Li loading in both cases. The difference in the performance of these two similar catalyst systems could be traced to the preparation methods [Wang et al., 1995]. And there is a report [Seo et al., 1995] that the yield of C₂ hydrocarbons increased because many basic sites of O⁻ ions were

produced on the catalytic surface as the proton, H^+ , was eliminated from the OH^- . According to the report, it is clear to enhance the catalytic activity for ethylene production by adding MgO to the YSZ support.

Another interesting observation is that LiCl supported on MgO-YSZ composite displays higher activity as well as selectivity, with ethylene yield exceeding 63%. Addition of MgO has increased conversion, while maintaining selectivity.

2. Effect of Promoters

The addition of Mn to LiCl/MgO-YSZ has improved activity to 88%, and lowered the reaction temperature to 650 °C, but at the expense of selectivity. Mn-based catalyst systems are reported to be active for ODE, its variable oxidation states being responsible. One of the earliest known Mn-based systems, $Na_4P_2O_7-MnO_x/SiO_2$ patented by ARCO [Jones et al., 1988] and Phillips [Eastman and Kolts, 1983], is known to be highly active for ODE in cyclic mode of operation. Besides, LiCl/MnO₂ [Otsuka et al., 1986] and Mn-Na₂WO₄/SiO₂ [Kou et al., 1998] systems, which are active for OCM are known to be equally active for ODE. It is reported that Mn-O lattice helps in oxygen transport [Pak et al., 1996], through Mn^{2+}/Mn^{3+} redox pair, the role of alkali being to disperse and stabilize Mn against deep reduction [Mariscal et al., 1994]. In the present case, Mn could improve the oxygen transport characteristics of YSZ, leading to an increase in activity.

Addition of Sn increases activity as well as selectivity. Sn is a known promoter for ODE in Li⁺-Mg-O system. Conway et al. [1991] and Swaan et al. [1992] observe an increase in activity and a decrease in selectivity. For the Sn addition in Pt/Al₂O₃ during catalytic reforming [Sunee et al., 2003], the presence of Sn improved the catalyst resistance to deactivation and inhibited the formation of highly dehydrogenated surface species that were intermediates for coking. Exact mode of promotion by Sn is not known at present. For OCM reaction, van Keulen et al. [1992] report the formation of a ternary phase, Li₂Mg₂SnO₆ in Li-Mg-Sn-O system. This phase retards the loss of Li, especially in OCM reaction. In the present case, with the loading of Sn around 9 wt%, formation of the ternary phase could not be ruled out, though no evidence to this effect has been gathered as of now.

Fig. 2 shows catalytic activity of Li-Mn-Sn/MgO-YSZ. The catalyst takes the highest ethylene yield of 65% and exhibits good stability for more than 4 h. If the ethylene selectivity is further improved by the impregnation of a proper promoter, the Li-Mn-Sn/MgO-YSZ

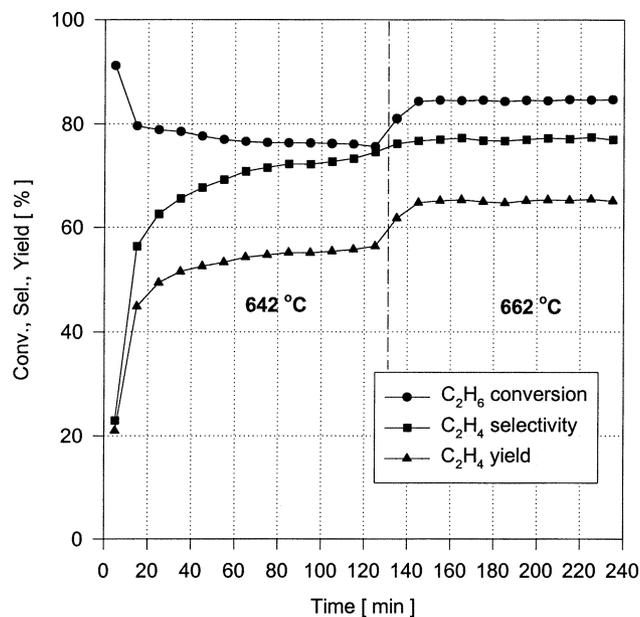


Fig. 2. Oxidative ethane dehydrogenation activity as a function of time on stream over LiCl-Mn-Sn/YSZ. Reaction conditions: 0.5 g catalyst, C₂H₆ : O₂ : N₂=1 : 1 : 8, flowrate=30 ml/min, T=642-662 °C.

catalyst system can be considered a good candidate for ODE.

3. Use of Li₂O Instead of LiCl

Considering the corrosive nature of LiCl and its gradual loss during reaction, formulations based on Li₂O were prepared and evaluated. The results of Li₂O based catalysts are shown in Table 2. Li₂O/MgO shows less activity and high selectivity in the absence of YSZ. Changing the support to MgO-YSZ improves activity at the expense of selectivity. Addition of Sn leads to very high selectivity. Li₂O-Mn-Sn/MgO-YSZ shows good conversion and high selectivity with ethylene yields >60% and shows better performance in comparison with similar catalyst systems (Li-Sn/MgO) reported earlier [Swaan et al., 1992]. However, the yield decreases from 60% to 55% over a period of 8 h. In general, use of Li₂O in the place of LiCl leads to lower activity and yields. Of all the Li salts, LiCl is observed to be the most effective one for ODE [Wang et al., 1999]. It appears that Cl⁻ ions are essential for better performance. However, both Li₂O and LiCl-based catalysts tend to deactivate slowly. Gradual loss of

Table 2. Performance of Li₂O/MgO-YSZ based catalysts for ODE

Catalyst	Temp. (°C)	C ₂ H ₆ conversion (%)	C ₂ H ₄ selectivity (%)	C ₂ H ₄ yield (%)
Li ₂ O/MgO	642	25	78	20
	662	33	80	27
Li ₂ O/MgO-YSZ	642	47	62	29
	662	54	63	34
Sn-Li ₂ O/MgO-YSZ	642	32	96	31
	662	42	96	40
Sn-Mn-Li ₂ O/MgO-YSZ	642	65	84	55
	662	72	84	60(4 h)
	662	63	86	55(8 h)

Catalyst; 0.5 g, Feed; 10% C₂H₆, 10% O₂, 80% N₂, Flowrate; 30 ml/min.

LiCl and changes in the oxidation state of Mn are the possible reasons. Characterization of used catalysts is in progress to understand the mode of deactivation.

CONCLUSIONS

YSZ either alone or in combination with MgO is found to be a good support for LiCl and Li₂O-based catalysts, which is useful for ODE. And Mn and Sn are good promoters for such catalyst systems. LiCl-based catalysts are more active than Li₂O-based systems, and especially Sn-Mn-LiCl/MgO-YSZ leads to 85% ethane conversion, 77% ethylene selectivity and 65% ethylene yield at 662 °C. The catalysts investigated undergo slow deactivation after 6-8 h. Further modifications with rare earth or other transition metal oxides could improve stability.

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