# Oxidative dehydrogenation of ethane and propane over Mn-based catalysts

Qingjie Ge, B. Zhaorigetu, Chunying Yu, Wenzhao Li and Hengyong Xu

*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*
E-mail: geqj@ms.dicp.ac.cn

Received 18 January 2000; accepted 2 June 2000

The catalytic performances of Mn-based catalysts have been investigated for the oxidative dehydrogenation of both ethane (ODE) and propane (ODP). The results show that a LiCl/$MnO_x$/PC (Portland cement) catalyst has an excellent catalytic performance for oxidative dehydrogenation of both ethane and propane to ethylene and propylene, more than 60% alkanes conversion and more than 80% olefins selectivity could be achieved at 650 °C. In addition, the results indicate that Mn-based catalysts belong to p-type semiconductors, the electrical conductivity of which is the main factor in influencing the olefins selectivity. Lithium, chlorine and PC in the LiCl/$MnO_x$/PC catalyst are all necessary components to keep the excellent catalytic performance at a low temperature.

**Keywords:** Mn-based catalysts, ethane, propane, oxidative dehydrogenation

## 1. Introduction

Oxidative dehydrogenation of light alkanes to light alkenes is always attractive in industrial and academic fields for its remarkable economic significance [1,2]. To date, although a great deal of research on the oxidative dehydrogenation catalysts for ethane and propane has been done, there are still some challenging problems to be solved, such as selection of catalysts operating at low temperatures [3–11]. In this work, we successfully prepared an excellent low-temperature catalyst for the oxidative dehydrogenation of both ethane (ODE) and propane (ODP) to ethylene and propylene. The relations between the structure components and catalytic activities of Mn-based catalysts have also been discussed in detail.

## 2. Experimental

### 2.1. Catalyst preparation

$MnCO_3$ was dried at 120 °C for 4 h, and then calcined at 600 °C for 3 h and 800 °C for 3 h to form $MnO_x$. 90 wt% $MnCO_3$ and 10 wt% PC (Portland cement, produced in Dalian, BET surface area of 5.1 $m^2/g$, mainly containing 64.0% CaO, 20.3% $SiO_2$, 5.8% $Al_2O_3$ and 4.9% $Fe_2O_3$) were fully mixed by grinding, and dried at 120 °C, then calcined at 600 °C for 3 h and 800 °C for 3 h.

LiCl/$MnO_x$, LiCl/$MnO_x$/PC, LiF/$MnO_x$/PC, $Li_2SO_4$/$MnO_x$/PC and $CaCl_2$/$MnO_x$/PC were prepared by impregnation of $MnCO_3$ or $MnCO_3$/PC (particle size of 20–40 mesh) with a comparable volume of LiCl, LiF, $Li_2SO_4$ or $CaCl_2$ solution, respectively. The soaked samples were dried at 120 °C for 4 h, and calcined at 600 °C for 3 h and 800 °C for 3 h. In catalyst samples, the molar ratio of Mn to Li (or Ca) is 3.0.

### 2.2. Catalyst testing

The ODE and ODP reactions were carried out in a fixed-bed quartz microreactor at atmospheric pressure with 0.2 and 0.5 g catalyst loading, respectively. A mixture gas of ethane or propane, oxygen and helium was passed through the reactor. The feed and the product gases were analyzed on line by a gas chromatograph (Type 102-G, Shanghai, TCD detector) with C-molecular sieve columns for $O_2$, $N_2$, CO, and a gas chromatograph (103-G, Shanghai, TCD detector) with a Porapak column for CO, $CO_2$, methane, ethane, ethylene, propane and propylene.

### 2.3. Catalyst characterization

The phase compositions of the catalysts were determined by X-ray diffraction (XRD, D-MAX, Rigaku). The specific surface areas of the catalysts were measured and calculated according to the BET method.

For electrical conductivity measurements, the calcined catalyst was powdered and pressed into a disk of 10 mm in diameter and 1 mm in thickness. The catalyst disc was mounted in a quartz vessel and connected with two Pt disc electrodes on each side. The conductivity dependence on oxygen partial pressure was measured in a mixture of $N_2$ and $O_2$ with various ratios by using a 8840A multifunction meter.

## 3. Results and discussion

### 3.1. ODE reaction over Mn-based catalysts

A blank test carried out in the reactor loaded with only quartz sand showed that the non-catalytic contribution for ethane conversion at 650 °C was only 0.2%.

Table 1
The results of ODE reaction over Mn-based catalysts.[a]

| Catalyst | Conv. $C_2H_6$ (%) | Selectivity (mol%) | | | | Yield $C_2H_4$ (%) |
|---|---|---|---|---|---|---|
| | | CO | $CH_4$ | $CO_2$ | $C_2H_4$ | |
| Quartz sand | 0.2 | – | – | 100 | – | – |
| $MnO_x$ | 24.6 | 0.6 | 1.3 | 64.0 | 34.1 | 8.4 |
| LiCl/$MnO_x$ | 14.8 | – | – | 37.8 | 62.2 | 9.2 |
| $MnO_x$/PC | 34.3 | – | – | 85.2 | 14.8 | 5.1 |
| LiCl/$MnO_x$/PC | 66.1 | 3.6 | 2.7 | 6.3 | 87.4 | 57.8 |
| LiF/$MnO_x$/PC | 2.5 | – | – | 31.5 | 68.6 | 1.7 |
| $Li_2SO_4$/$MnO_x$/PC | 15.8 | – | 1.2 | 60.7 | 38.2 | 6.0 |
| $CaCl_2$/$MnO_x$/PC | 46.9 | 4.0 | 2.9 | 29.2 | 63.9 | 30.0 |

[a] Reaction conditions: 650 °C, 6000 $h^{-1}$, $C_2H_6/O_2/He = 19/11/70$.

Table 2
XRD and BET characterization results of Mn-based catalysts.

| Catalyst | XRD crystalline phase | Specific surface area ($m^2$/g) |
|---|---|---|
| $MnO_x$ | $Mn_2O_3$, $Mn_3O_4$ | 1.7 |
| $MnO_x$/PC | $Mn_2O_3$ | 3.6 |
| LiCl/$MnO_x$ | $Mn_2O_3$, $LiMn_2O_4$ | 4.1 |
| LiCl/$MnO_x$/PC | $Mn_2O_3$, $LiMn_2O_4$ | 4.2 |

In table 1, it is indicated that the LiCl/$MnO_x$/PC gave a high catalytic performance for ODE to ethylene at 650 °C, i.e., 66.1% ethane conversion, 87.4% ethylene selectivity and 57.8% ethylene yield; the results have been reproduced several times.

Addition of LiCl to the $MnO_x$/PC could dramatically increase both the ethane conversion and the ethylene selectivity. The ethylene yield reached 57.8%, which indicates that LiCl plays an important role in improving the catalytic performance, especially for ethylene selectivity. On the other hand, addition of PC to the LiCl/$MnO_x$ could remarkably increase the catalytic conversion of ethane from 14.8 to 66.1%, which demonstrates that PC is a necessary component for improving the low-temperature activity of the catalyst.

The influence of various salts of lithium was also studied. It was found that $Li_2SO_4$/$MnO_x$/PC has the lowest ethylene selectivity and LiF/$MnO_x$/PC has the lowest ethane conversion, while LiCl/$MnO_x$/PC shows the highest ethane conversion and ethylene selectivity. When LiCl was substituted by $CaCl_2$ in the catalyst systems, conversion, selectivity and yield decreased from 66.1, 87.4 and 57.8% to 46.9, 63.9 and 30.0%, respectively.

It seems that there exists a synergistic effect between the Cl, Li and the PC components of LiCl/$MnO_x$/PC, the reason of which will be further studied.

XRD characterization results (table 2) exhibit that the existence of a $LiMn_2O_4$ phase maintains the high ethylene selectivity of catlysts, while the $Mn_2O_3$ phase is the necessary active phase for catalysts to keep high catalytic performance.

From table 2, it is shown that the specific surface areas of $MnO_x$, $MnO_x$/PC, LiCl/$MnO_x$ and LiCl/$MnO_x$/PC are between 1.5 and 4.5 $m^2$/g, the addition of PC to LiCl/$MnO_x$ having no evident influence on the specific area. The results indicate that the dispersion of $MnO_x$ is not likely a main factor of affecting the activity of catalysts.

Table 3
The electrical conductivity of Mn-based catalysts under pure oxygen.

| Sample | $MnO_x$ | $MnO_x$/PC | LiCl/$MnO_x$ | LiCl/$MnO_x$/PC |
|---|---|---|---|---|
| $\log\sigma$ (s/m) | −0.94 | −1.12 | −0.70 | −0.74 |

The results of electrical conductivity measurements showed that $MnO_x$, $MnO_x$/PC, LiCl/$MnO_x$ and LiCl/$MnO_x$/PC were all p-type semiconductors, as their electrical conductivity ($\log\sigma$) is proportional to the oxygen partial pressure of the mixed gases [12]. Table 3 presents their electrical conductivity ($\log\sigma$) under pure oxygen at 650 °C, and combining with the results obtained in table 1, we can conclude that with the addition of LiCl to $MnO_x$ and $MnO_x$/PC, the electrical conductivity ($\log\sigma$) of the samples increased, and the number of the oxygen vacancies of the catalyst increased. The oxygen vacancies ($V_O^{\cdot\cdot}$) could react with oxygen to form non-fully reduced oxygen species ($O^{\delta-}$) as follows:

$$V_O^{\cdot\cdot} + \tfrac{1}{2}O_2 \rightarrow O^{\delta-} + h^{\cdot}$$

Such oxygen species are thought to be the main factor of influencing the ethylene selectivity [13,14]. Therefore, ethylene selectivity increased respectively from 34.1 and 14.8% to 62.2 and 87.4% as LiCl was added into $MnO_x$ and $MnO_x$/PC. When PC was added into $MnO_x$ and LiCl/$MnO_x$, the electrical conductivity decreased. However, the LiCl/$MnO_x$/PC catalyst does not show lower selectivity than the LiCl/$MnO_x$ catalyst, the reason of which could be the synergistic effect existing in LiCl/$MnO_x$ and PC. In addition, when PC was added into $MnO_x$ and LiCl/$MnO_x$, the dispersion of the $MnO_x$ increased, thus the active sites on the surface were also increased, and this in turn increased the ability to activate ethane, resulting in an increase of ethane conversion from 24.6 to 34.3% or from 14.8 to 66.1%, respectively.

Table 4 shows the results of the change of reaction conditions over the LiCl/$MnO_x$/PC sample. It could be seen that: (1) all the ethane conversions, ethylene selectivities and ethylene yields increased as reaction temperature increased from 500 to 650 °C; (2) as the ratio of ethane to oxygen decreased from 3.1 to 1.6 and the GHSV from 6000 to 15 000 $h^{-1}$, the ethane conversion remarkably increased, while ethylene selectivity decreased slightly; (3) a 73.3% ethane conversion, 87.0% ethylene selectivity and 63.8% ethylene yield could be achieved at 650 °C, 6000 $h^{-1}$ and $C_2H_6/O_2/He = 18.6/11.4/70.0$ (mol%).

### 3.2. ODP reactions over the LiCl/$MnO_x$/PC catalyst

Catalytic testing of the LiCl/$MnO_x$/PC catalyst for the ODP reaction has also been investigated under the reaction conditions of 6000 $h^{-1}$, $C_2H_6/O_2/N_2 = 22/11/67$ (mol%). The results are shown in figure 1.

Table 4
Effects of ODE reaction conditions on LiCl/MnO$_x$/PC catalyst properties.

| React. temp. (°C) | GHSV ($h^{-1}$) | $C_2H_6/O_2$ | Conv. $C_2H_6$ (%) | Selectivity (mol%) | | | | | Yield $C_2H_4$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | CO | $CH_4$ | $CO_2$ | $C_2H_2$ | $C_2H_4$ | |
| 650 | 6000 | 1.6 | 73.3 | 4.5 | 1.8 | 6.7 | – | 87.0 | 63.8 |
| 650 | 6000 | 1.7 | 66.1 | 3.6 | 2.7 | 6.3 | – | 87.4 | 57.8 |
| 650 | 6000 | 2.2 | 47.5 | 2.3 | 2.2 | 5.5 | 0.9 | 89.2 | 42.4 |
| 650 | 6000 | 2.4 | 46.1 | 1.9 | 1.7 | 5.3 | 0.4 | 90.7 | 41.8 |
| 650 | 6000 | 3.1 | 39.5 | 2.1 | 1.8 | 4.9 | – | 91.2 | 36.0 |
| 650 | 6000 | 2.2 | 47.5 | 2.3 | 2.2 | 5.5 | 0.9 | 89.2 | 42.4 |
| 650 | 9000 | 2.2 | 29.6 | – | 2.7 | 4.0 | – | 93.3 | 27.6 |
| 650 | 12000 | 2.2 | 15.5 | – | 0.9 | 5.1 | – | 94.1 | 14.6 |
| 650 | 15000 | 2.2 | 14.1 | – | 0.8 | 3.4 | – | 95.9 | 13.6 |
| 650 | 6000 | 2.4 | 46.1 | 1.9 | 1.7 | 5.3 | 0.4 | 90.7 | 41.8 |
| 600 | 6000 | 2.4 | 30.2 | 2.2 | 1.3 | 8.2 | 1.4 | 86.9 | 26.3 |
| 550 | 6000 | 2.4 | 17.5 | 7.6 | 0.9 | 32.3 | 1.4 | 57.8 | 10.1 |
| 500 | 6000 | 2.4 | 3.4 | – | – | 100 | – | – | – |

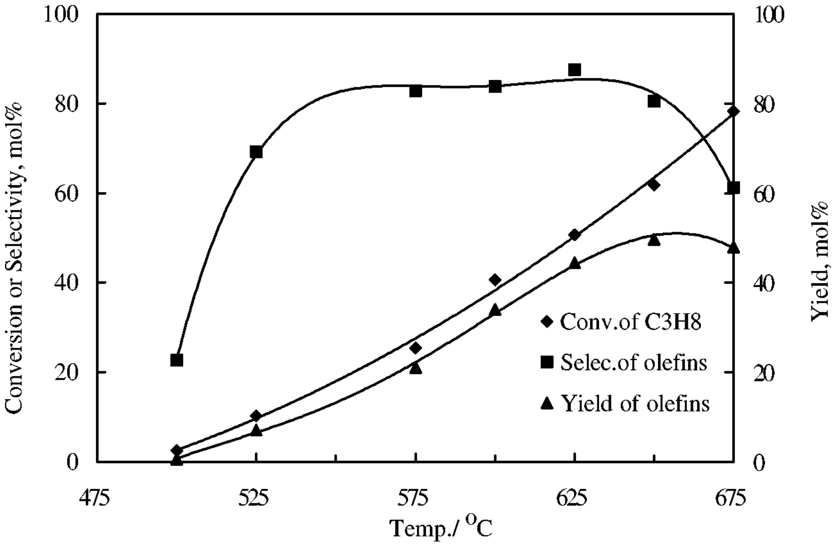

Figure 1. ODP reaction to ethylene and propylene over LiCl/MnO$_x$/PC catalyst.

Table 5
ODP reaction to ethylene and propylene at 650 °C.

| Catalyst | Conv. $C_3H_8$ (mol%) | Selectivity (mol%) | | | | | Yield $C_2^=-C_3^=$ [a] (%) |
|---|---|---|---|---|---|---|---|
| | | CO | $CO_2$ | $CH_4$ | $C_2H_6$ | $C_2^=-C_3^=$ | |
| Blank reaction | 48.0 | 17.0 | 5.2 | 5.4 | 2.7 | 69.7 | 33.5 |
| LiCl/MnO$_x$/PC | 61.8 | 6.5 | 5.6 | 3.9 | 3.6 | 80.4 | 49.7 |

[a] $C_2^=-C_3^=$ – ethylene and propylene.

Figure 1 shows that propane conversion increased from 2.5 to 78.3% as the reaction temperature increased from 500 to 675 °C, while olefins selectivity increased sharply to more than 80% at about 550 °C, and then remained stable until 650 °C and finally decreased, with the olefins yield reaching the maximum (49.7%) at 650 °C. These results indicate that LiCl/MnO$_x$/PC is also a good catalyst for the ODP reaction to ethylene and propylene, and the optimal temperature is 650 °C. 61.8% propane conversion, 80.4% light olefins selectivity and 49.7% light olefins yield could be obtained under proper reaction conditions.

In addition, we also evaluated the non-catalytic reaction behaviour of ODP to ethylene and propylene at 650 °C, which was the optimal temperature for the ODP catalytic reaction (table 5). The results illustrate that the non-catalytic reaction gives 48.0% propane conversion and 69.7% olefins selectivity. Compared with the catalytic reaction of ODP over LiCl/MnO$_x$/PC, the conversion decreased by 13.8%, while the light olefins selectivity decreased by 10.7%. Such results indicate that the ODP catalytic reaction over LiCl/MnO$_x$/PC has improved the reaction performance as compared with the non-catalytic reaction. Especially, the light olefins yield has enhanced from 33.5 to 49.7%.

Considering the above results of the ODE and ODP reactions, it could be concluded that LiCl/$MnO_x$/PC catalysts have excellent catalytic performances not only for the ODE reaction to ethylene, but also for the ODP reaction to ethylene and propylene. Such kind of catalysts is very useful for the conversion and utilization of industrial gases, including both ethane and propane.

## 4. Conclusion

(1) The LiCl/$MnO_x$/PC catalyst has excellent catalytic performances for the oxidative dehydrogenation of both ethane to ethylene and propane to ethylene and propylene. For the ODE reaction, an ethane conversion of 73.2%, an ethylene selectivity of 87.0% and an ethylene yield of 63.8% were achieved under the reaction conditions of 650 °C, 6000 $h^{-1}$, and $C_2H_6/O_2/He = 18.6/11.4/70.0$ (mol%). For the ODP reaction: 61.8% propane conversion, 80.4% ethylene and propylene selectivity and 49.7% ethylene and propene yield could be obtained at 650 °C, 6000 $h^{-1}$, $C_2H_6/O_2/N_2 = 22/11/67$ (mol%).

(2) The optimal ODE reaction conditions are $C_2H_6/O_2 = 1.6–1.2$, 650 °C, 6000 $h^{-1}$ and the suitable ODP reaction temperature is 650 °C.

(3) Mn-based catalysts belong to p-type semiconductors, their electrical conductivity (oxygen hole number) is the main factor in influencing the olefins selectivity. In the LiCl/$MnO_x$/PC catalyst, Li, Cl and PC are all necessary to keep excellent catalytic performance at a low temperature, and there seems to exist a synergistic effect between the LiCl/$MnO_x$ and PC components.

## References

[1] H.H. Kung, Adv. Catal. 40 (1994) 1.
[2] M. Baerns and O. Buyevskaya, Catal. Today 45 (1998) 13.
[3] H. Swan, A. Toebes, K. Seshan, J.G. Van Ommen and J.R.H. Ross, Catal. Today 13 (1992) 629.
[4] E.M. Thorsteinson, T.P. Wilson, F.G. Young and P.H. Kasai, J. Catal. 52 (1978) 116.
[5] T. Chen, W. Li, C. Yu and G. Xu, J. Nat. Gas Chem. 7 (1998) 283.
[6] J. El-Idrissi, M. Kacimi, F. Bozon-Verduraz and M. Ziyad, Catal. Lett. 56 (1998) 221.
[7] P. Michalakos, M.C. Kung, I. Jahan and H.H. Kung, J. Catal. 140 (1993) 226.
[8] Q. Ge, C. Yu, W. Li and H. Xu, Tianranqi Huagong (China) 24 (1999) 21.
[9] S. Wang, K. Murata, T. Hayakawa, S. Hamakawa and K. Suzuki, Chem. Lett. (1999) 25.
[10] D. Sam, V. Soenen and J.C. Volta, J. Catal. 123 (1990) 417.
[11] M.C. Kung, J. Catal. 134 (1992) 668.
[12] Z. Zhang, X.E. Verykios and M. Baerns, Catal. Rev. Sci. Eng. 36 (1994) 507.
[13] T. Chen, W. Li and C. Yu, Chin. J. Catal. 19 (1998) 37.
[14] T. Chen, W. Li, C. Yu, Y. Ji and Z. Yu, Chem. J. Chin. Univ. 17 (1996) 1617.