Oxidative Dehydrogenation of Ethane to Ethylene over LiCl/MnO_x/PC Catalysts†

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The catalytic stability of LiCl/MnO_x/PC catalyst have been investigated, the deactivation mechanism was discussed. The experimental results show that ethane conversion decreases and ethylene selectivity keeps about 90% as reaction time increases. The main deactivation reasons of LiCl/MnO_x/PC catalyst for oxidative dehydrogenation of ethane (ODHE) to ethylene are the transition of active species Mn_2O_3 to MnO species and the loss of active component Cl in catalyst. Instead of ethane with FCC tailed-gas, the stability of LiCl/MnO_x/PC catalyst has been largely improved.

Keywords Ethane, oxidative dehydrogenation, ethylene, LiCl/MnO_x/PC catalyst

Introduction

The selective oxidation of light alkanes into their corresponding alkenes is always desirable and has attracted much attention.[1] As one of natural gas major components, ethane conversion and utilization exists a growing interest in many fields, especially for ethylene synthesis.[2-5] Up to date, the steam cracking of ethane is still considered to be a conventional method for ethylene production. The oxidative dehydrogenation of ethane (ODHE) to ethylene has become an attractive alternative in recent decade.[6-9] The overall reaction for steam cracking and oxidative dehydrogenation of ethane to ethylene can be written as follows:

$$C_2H_6 = C_2H_4 + H_2 \text{ (endothermic reaction)}$$
$$\Delta H^0_{298} = 136 \text{ kJ·mol}^{-1} \quad (1)$$

$$C_2H_6 + 1/2\ O_2 = C_2H_4 + H_2O \text{ (exothermic reaction)}$$
$$\Delta H^0_{298} = -105 \text{ kJ·mol}^{-1} \quad (2)$$

Many efforts have been paid for the development of new catalysts for oxidative dehydrogenation of ethane (ODHE) to ethylene in recent years.[10-19] Some catalysts like $SrFeO_{3-\delta}Cl_\sigma$,[15] LiCl/$SO_4^{2-}$-$ZrO_2$,[16] LiCl/$MnO_x$/PC (Portland Cement),[17] $YBa_2Cu_3O_{7-\sigma}X_\sigma$,[18] were reported to have shown excellent low-temperature catalytic performance for ODHE reaction to ethylene. However, the catalytic stability of these catalysts is still a challenge subject for their further application. Therefore, in this paper, the catalytic stability of LiCl/MnO_x/PC catalyst have been investigated, the deactivation mechanism were discussed using characterization method like XRD, TG and EA (Element Analysis) combining with activity testing results.

Experimental

LiCl/MnO_x/PC were prepared by impregnation of $MnCO_3$/PC (particle size of 20—40 mesh) with a comparable volume of LiCl solution. The soaked samples were dried at 120℃ for 4 h, and calcined at 600℃ for 3

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Received September 4, 2000; accepted November 6, 2000.
† Special paper from the "*China-Netherlands Bilateral symposium on Organometallic Chemistry and Catalysis*", Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China, 1999.
Project supported by the key project of Chinese Academy of Sciences. (No. KY951-A1-201-5).

h and 800℃ for 3 h. In catalyst samples, the molar ratio of Mn to Li is 3.0.

ODHE to ethylene reaction were carried out in a fixed-bed quartz micro-reactor at atmospheric pressure with 0.2 g catalyst loading. A mixture gas of ethane, 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.

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.

CO_2 pulse adsorption (CPA): Put 0.2 g catalyst into 1 mL sample tubes, increasing temperature to 650℃ in Ar atmosphere (35 mL/min) and keep 30 min. Pulse CO_2 and record the signal of chromatographic peak. Calculate the relative adsorption I (see the following formula).

$$I(\%) = \sum(1 - I_i/I_0) \times 100\%$$

I_i represents the signal value of the Ith times pulse, I_0 represents the signal value of saturated adsorption value.

CO_2 temperature programmed desorption (CO_2 - TPD): decrease temperature of the catalyst samples in CO_2-pulse experiments from 650℃ to 100℃, switch Ar to CO_2 for 20 min, switch to Ar again. After the chromatographic signal steady, TPD were carried out. the rate is 15℃/min.

Li content in catalyst was determined by IRIS-Plasma, which produced by TJA(Thermo-Jarrell Ash) company; Cl content in catalyst was determined by chemical analysis: catalysts were dissolved by nitric acid and were titrated by standard $AgNO_3$ solution using $K_2Cr_2O_7$ indicator.

Thermal gravity analysis (TGA) were carried out at Perkin-Elmer TGS-2 apparatus, collecting and dealing with data using Perkin-Elmer 3600 database. Increasing temperature was in air with 10 K/min rates.

Results and discussion

420 min experimental results of ODHE *to ethylene over* $LiCl/MnO_x/PC$ *catalysts*

Fig. 1 shows the experimental results of ODHE to ethylene under the conditions of 650℃, 6000 h^{-1}, and $C_2H_6/O_2/He = 18.6/11.4/70.0$ (mol%) over 0.2 g $LiCl/MnO_x/PC$ catalysts. It was exhibited that ethane conversion decreased and ethylene selectivity keep at about 90% during the reaction time.

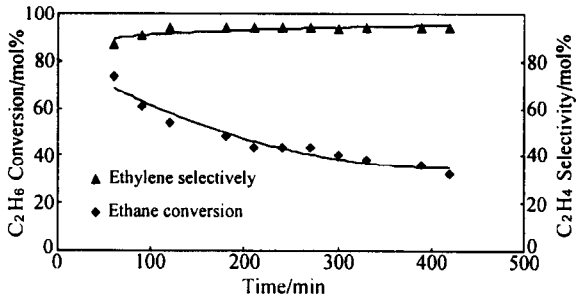

Fig. 1 The 420-min experimental results of ODHE to ethylene over $LiCl/MnO_x/PC$.

Characterization of catalysts

To discuss the reasons of catalyst deactivation, some characterizations of catalysts have been carried out using XRD, CPA, CO_2-TPD, TGA, BET surface areas, and electrical conductivity measurement.

XRD characterizations (Fig. 2) exhibit that the main active phases are Mn_2O_3 and $LiMn_2O_4$ in fresh catalysts, while after the 420 min reaction, partial Mn_2O_3 peak disappear and MnO new peaks are formed, $LiMn_2O_4$ active phase keep unchanged. Combined with activity testing results, it is indicated that $LiMn_2O_4$ is active species for keep high ethylene selectivity and Mn_2O_3 is important for catalyst keeping high conversion. Mn_2O_3 phase transition to MnO is one main reason of catalyst deactivation. In addition, XRD peak intensity of

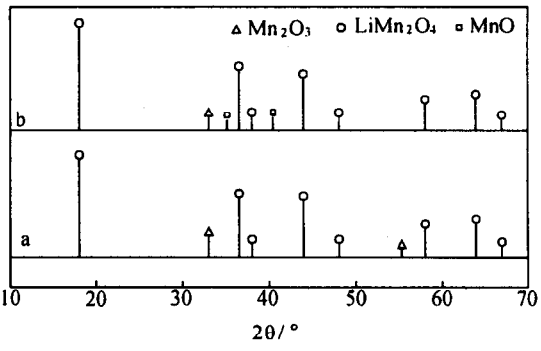

Fig. 2 XRD spectra of $LiCl/MnO_x/PC$ catalyst before (a) and after (b) reaction.

catalyst has no evident change before and after reaction, which exhibits that crystal growth is not the main reason of catalyst deactivation.

Table 1 and Fig. 3 show the results of CO_2 adsorption and CO_2-TPD of $LiCl/MnO_x/PC$ catalysts. They exhibited that: at 923 K(650℃), the amount of CO_2 adsorption is very little, and could reach equilibrium promptly; The desorption-peak of CO_2 is weak, which appears is at 500 K (227℃). All above results show that high ethylene selectivity in reaction at 650℃ really comes from the catalytic behavior of $LiCl/MnO_x/PC$ catalyst, rather than a gloss caused by the adsorption of CO_2 on the basic catalyst. This result is corresponding to the activity testing results.

Table 1 Pulse CO_2-adsorption result of $LiCl/MnO_x/PC$ catalyst at 650℃

Pulse number	1	2	3	4	5	6	7
I_i/I_0	0.990	0.995	0.997	0.999	1.000	1.000	1.000
I (%)	1.0	1.5	1.8	2.0	2.0	2.0	2.0

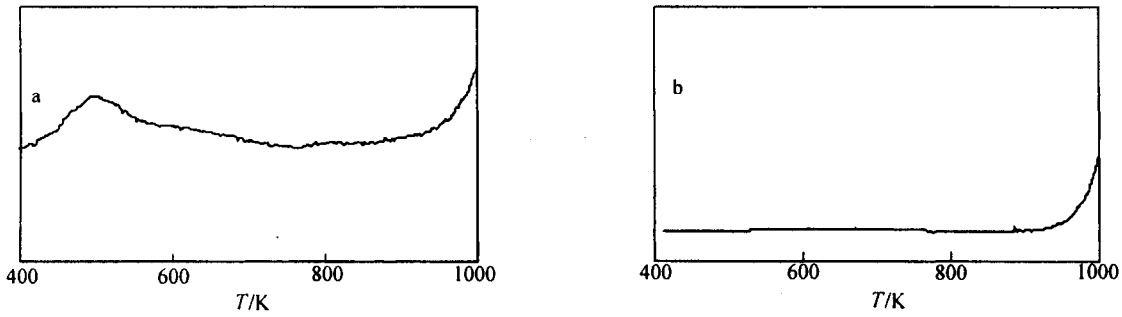

Fig. 3 TPD spectra of $LiCl/MnO_x/PC$ (a. CO_2-TPD; b. Blank-TPD).

Table 2 Li, Cl content and BET surface area of $LiCl/MnO_x/PC$ before and after reaction

	Li (w/%)	Cl (w/%)	BET surface area (m^2/g)
Before reaction	2.44	2.03	4.2
After reaction 420 min	2.46	0.27	3.6

Table 2 listed the content of Li and Cl, BET surface area of $LiCl/MnO_x/PC$ catalyst before and after reaction. The results indicate that Li has no loss for $LiMn_2O_4$ structure and Cl loss is the main reason of catalyst deactivation, this is the same as the conclusion of XRD characterization results. This inspire us imagining that stabilizing the content of Cl in fresh catalyst, Cl substituting O enter the structure of $LiMn_2O_4$ may be an effecting method. This will be research in further. BET surface areas of catalyst before and after reaction reveals also that crystal growth is not the main reason for catalyst deactivation.

TGA characterization results (Fig. 4) show the another aspects that $LiCl/MnO_x/PC$ has no evident carbon deposition during 420-min reaction of ODHE to ethylene.

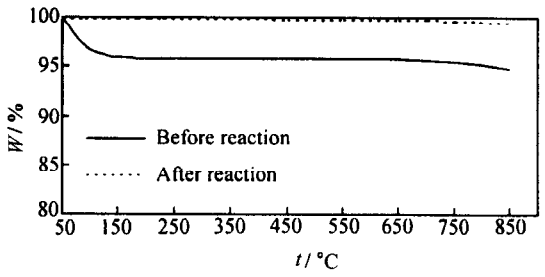

Fig. 4 TGA curves for $LiCl/MnO_x/PC$ catalyst.

Modification of catalytic stabilization of $LiCl/MnO_x/PC$ *catalysts for* ODHE *to ethylene*

From above experiments, we found that the main reasons of catalyst deactivation are the transition of Mn_2O_3 active species to the new species, *i. e.* MnO, and Cl loss of catalyst in reaction. So, to improve the stability of catalyst, inhibiting Mn_2O_3 phase transition and Cl loss of catalyst have to be resolved. These prob-

lems may be solved by changing the feed gases, such as adding gases including Cl. However, It is not feasible to add gases including Cl into the feed gases because of environmental requirements. In this paper, FCC tailed-dry gas was used to substitute ethane for ODHE reaction to ethylene, the feed gases composition is: 24.0% C_2H_6 + 11.8% O_2 + 12.3% N_2 + 20% H_2 + 28.1% CH_4 + 1% CO + 2.4% CO_2 + 0.4% C_2H_4. To our surprise, the catalytic stability of $LiCl/MnO_x/PC$ catalysts for oxidative dehydrogenation of FCC tailed-gas to ethylene was largely improved under the reaction of 650℃, 6000 h^{-1} compared to those of ODHE to ethylene (Fig. 5), the reasons of which are to be researched further.

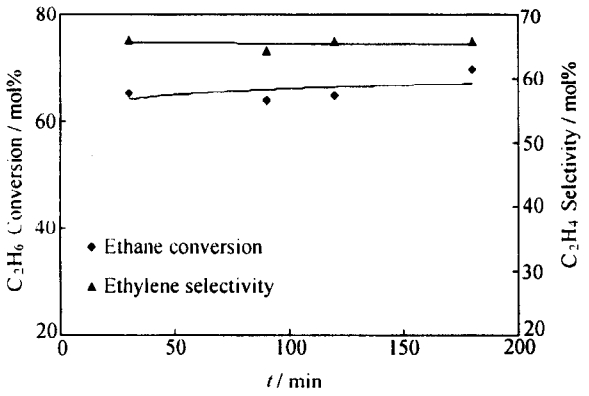

Fig. 5 The 180-min experimental results of FCC tailed-gas oxidative dehydrogenation to ethylene over $LiCl/MnO_x/PC$.

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(E200009183 LI, L.T.; LING, J.)