Lithium-chloride-promoted sulfated zirconia catalysts for the oxidative dehydrogenation of ethane

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Received 11 November 1998; accepted 26 March 1999

The oxidative dehydrogenation of ethane over sulfated-zirconia-supported lithium chloride catalysts has been systematically investigated. The optimal experimental parameters were obtained. It is found that sulfation of zirconia increases the catalytic activity. 2–3.5 wt% lithium chloride on sulfated zirconia catalysts exhibit high catalytic activity for oxidative dehydrogenation of ethane, with particularly high activity for ethene production. 70% selectivity to ethene at 98% ethane conversion, giving 68% ethene yield, is achieved over 3.5 wt% LiCl/SZ at 650 °C.

Keywords: oxidative dehydrogenation, ethane, sulfated zirconia, lithium chloride

1. Introduction

The catalytic oxy-dehydrogenation of light alkanes to olefins is a very important chemical process. The oxidative dehydrogenation (ODH) of ethane, as one of the second reactions in the oxidative dehydrogenation of methane, has been extensively studied over the past years. Several oxide catalyst systems such as V–Mo–O, Li/MgO and rare earth oxides are found effective for this reaction [1–3]. Among them, the most successful catalyst is Li/MgO modified with Cl^- ions. An ethene yield of 50% could be achieved [4]. However, few work has been concentrated on the zirconia system.

It has been reported that some oxidative coupling of methane (OCM) catalysts also show good catalytic activity in the oxidative dehydrogenation of ethane [4,5]. Some researchers have found that alkali-metal-promoted zirconia catalysts exhibited high activity in the oxidative coupling of methane [6,7]. We recently have also reported the excellent performance of Li-doped sulfated zirconia in the oxidative coupling of methane [8]. The oxidative coupling of methane to C_2 hydrocarbons is inevitably accompanied by the concurrent conversion of ethane to ethene. In this paper, we report the results of various zirconia-supported lithium catalysts for the oxidative dehydrogenation of ethane into ethene.

2. Experimental

2.1. Catalyst preparation and characterization

$Zr(OH)_2$ was precipitated from a $ZrONO_3$ solution by drop-wise adding $NH_3\cdot H_2O$. After drying at 105 °C, $Zr(OH)_2$ was calcined at 300 °C for 3 h and then continued to be calcined at 700 °C for 3 h. The sulfated zirconia (SZ) with 6 wt% sulfate was prepared by wetness impregnation with $(NH_4)_2SO_4$ at an appropriate concentration, dried at 105 °C and calcined at 700 °C for 3 h. The resultant SZ samples were impregnated with lithium ions solution at the required concentration by the method described above. A commercial Li_2ZrO_3 obtained from Soekawa Chemicals was also used as a catalyst in this investigation.

The BET surface area was measured by nitrogen adsorption at -196 °C on a Micromeritics volumetric equipment provided by Shimadzu. Before adsorption, the samples were degassed under high vacuum at 200 °C for 2 h. XRD measurements were conducted on a Philips PW 1800 X-ray diffractometer at 40 kV, and 40 mA. The radiation used was Cu $K\alpha$ with a Ni filter.

2.2. Catalytic evaluation

The selective oxidative dehydrogenation of ethane was carried out at atmospheric pressure in a fixed-bed vertical-flow reactor constructed from a high-purity alumina tube (i.d. = 6 mm) packed with 1 g catalysts and 2 g quartz sand. The feed consisting of 10% ethane, 10% oxygen and 80% nitrogen was introduced into the reactor at a flow rate of 60 ml/min. The reactants and products were analyzed by two on-line gas chromatographs (GC-8A) equipped with a Porapak Q column using FID for hydrocarbons and a 5A molecular sieve column for CO, CO_2, CH_4, O_2, N_2, and H_2 using TCD, respectively. Tests with quartz sand and empty reactor revealed that the contribution from homogeneous reaction was negligible below 650 °C under the present conditions.

Table 1
Catalytic behavior of ethane ODH over zirconia-based catalysts at 650 °C.

Catalyst	S_{BET}	Conversion (%)		Selectivity (%)				Yield (%)
	(m^2/g)	C_2H_6	O_2	C_2H_4	CO	CO_2	CH_4	C_2H_4
ZrO_2	21.2	65.9	100	29.2	19.2	49.2	1.7	19.2
SZ	72.5	70.4	100	30.8	18.8	47.3	3.1	21.7
$LiCl/ZrO_2$	4.6	87.2	95.3	60.1	9.3	21.8	1.4	52.4
LiCl/SZ	2.0	97.6	96.3	69.8	11.9	14.3	1.7	68.1
Li_2ZrO_3	<1	20.3	15.1	83.3	8.0	8.0	0.7	16.9

3. Results

3.1. Catalytic performance of various catalysts

Table 1 presents the performance of ethane ODH over supports (ZrO_2 and SZ) and LiCl-based catalysts with 3.5 wt% Li as well as over the Li_2ZrO_3 catalyst. For zirconia and sulfated zirconia, ethane conversions are over 60% with ethene selectivity around 30%. However, sulfated zirconia exhibits slightly higher catalytic activity and selectivity to ethene. Doped lithium chloride on supports shows a positive effect on ethane conversion and selectivity to ethene. For $LiCl/ZrO_2$, ethane conversion is enhanced to 87%, while ethene selectivity is almost doubled. Similarly, ethane conversion and ethene selectivity over LiCl/SZ are also significantly improved with 70% selectivity at 98% conversion, giving 68% ethene yield. Like the behavior of the supports, LiCl/SZ also exhibits higher catalytic conversion and ethene selectivity than Li/ZrO_2. This suggests that sulfation of zirconia produces a promotion effect on catalytic activity and ethene selectivity. It has been found Li/SZ shows better catalytic performance than Li/ZrO_2 in the OCM reaction [8]. The other catalyst Li_2ZrO_3 shows the lowest catalytic activity, but the highest ethene selectivity. The ethene yield is even lower than that over the two supports.

Figure 1 shows the results of ethane ODH over Li/SZ catalysts prepared by different lithium precursor compounds (LiCl, LiF, $LiNO_3$ and Li_2CO_3). It is observed that ethane conversion and ethene selectivity are very similar over LiF/SZ and Li_2CO_3/SZ. Ethene selectivity decreases when ethane conversion increases as the temperature increases. For $LiNO_3$/SZ, ethane conversions are higher than those of LiF/SZ and Li_2CO_3/SZ at all temperatures. However, selectivities to ethene are relatively lower. Unlike the behavior of LiF/SZ and Li_2CO_3/SZ, ethene selectivity increases as the temperature increases. LiCl/SZ demonstrates the highest ethane conversion and still maintains the ethene selectivity as high as 90%. Ethene selectivity first increases at the lower temperatures and then decreases after 620 °C. The characteristics of catalytic activity over the four above catalysts suggests that the dominant reaction mechanism is different. For the four catalysts, ethene yield follows the sequence LiCl/SZ > $LiNO_3$/SZ > LiF/SZ > Li_2CO_3/SZ.

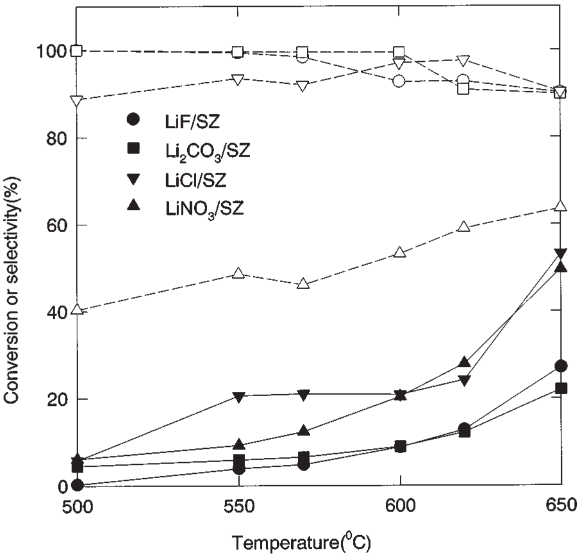

Figure 1. Catalytic activity of Li/SZ catalysts prepared from different lithium precursors. Solid symbols – C_2H_6 conversion; open symbols – C_2H_4 selectivity.

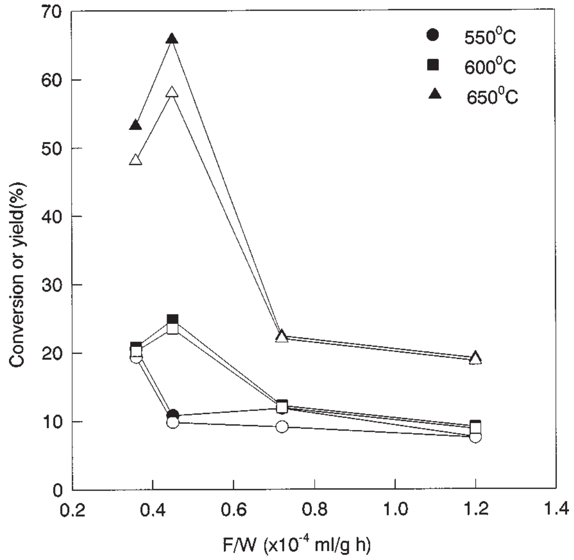

Figure 2. Effect of space velocity on catalytic activity of 5 wt% LiCl/SZ at different temperatures. Solid symbols – C_2H_6 conversion; open symbols – C_2H_4 yield.

The effect of space velocity on catalytic behavior over 5 wt% LiCl/SZ is presented in figure 2. As seen from the figure, ethane conversion and ethene yield exhibit the highest values at 4500 ml/g h at 600–650 °C, while the best value can be achieved at a space velocity of 3600 ml/g h at 550 °C. When space velocity is higher, the conversion and

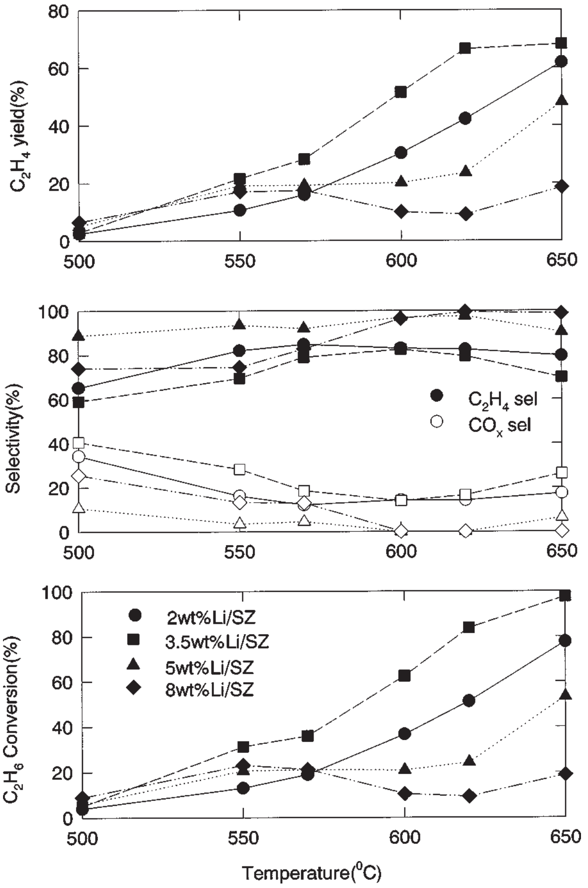

Figure 3. Catalytic activity of various LiCl/SZ catalysts as a function of temperature.

yield will decrease. Therefore, the optimal space velocity will be 3600–4500 ml/g h under the present conditions.

The dependence of activity, selectivity and yield of LiCl/SZ catalysts with different lithium contents on the reaction temperature is shown in figure 3. It can be seen that the reaction temperature and lithium loading have a significant effect on the catalytic behavior. Ethane conversion increases with increasing temperature over LiCl/SZ at lower lithium content (2–5 wt% Li), however, 8 wt% LiCl/SZ exhibits a complex behavior. At low temperature before 550 °C, ethane conversion increases with the temperature, then it shows a decreasing trend at the temperature range of 550–620 °C. After 620 °C, ethane conversion increases again. Among the catalysts, 3.5 wt% LiCl/SZ exhibits the highest ethane conversion at all temperatures. For ethene selectivity, the four catalysts present similar patterns, i.e., ethene selectivity increases first as the temperature increases and then decreases at higher temperatures. It is noted that 5–8 wt% LiCl/SZ catalysts generally produce higher ethene selectivity than 2–3.5 wt% LiCl/SZ catalysts. This is probably due to the lower ethane conversion on 5–8 wt% LiCl/SZ. Because of the similar pattern of ethene selectivity over all catalysts, the ethene yield over these catalysts shows the same variation pattern as that of ethane conversion. Therefore, 3.5 wt% LiCl/SZ is the best catalyst in terms of conversion, selectivity and yield.

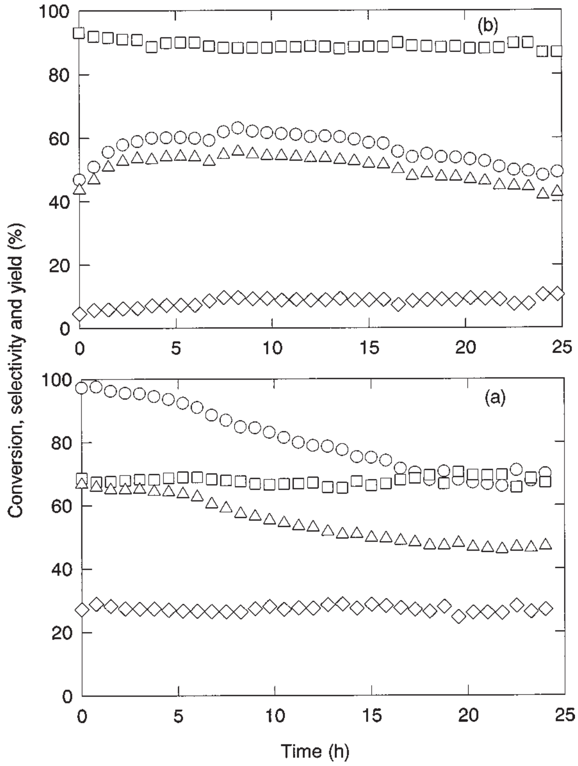

Figure 4. Catalytic behavior as a function of time over LiCl/SZ catalysts at 650 °C: (a) 3.5 wt% LiCl/SZ and (b) 5 wt% LiCl/SZ. (○) C_2H_6 conversion, (□) C_2H_4 selectivity, (◇) CO_x selectivity and (△) C_2H_4 yield.

Figure 4 shows the catalytic performance of 3.5 wt% LiCl/SZ and 5 wt% LiCl/SZ catalysts at 650 °C as related to the reaction time. It can be seen that the two catalysts present a different stability behavior. For 3.5 wt% LiCl/SZ ethane conversion and ethene yield decrease gradually within 15 h and then remain nearly unchanged thereafter. Ethane conversion and ethene yield change from 98 and 68 to 70 and 46%, respectively. Ethene and CO_x selectivities stay at the same level during 24 h testing. The ethane conversion and ethene yield over 5 wt% LiCl/SZ increase in the first 10 h and then show decreasing trends, however, the deactivation rates are much slower than those of 3.5 wt% LiCl/SZ. After 25 h testing, ethane conversion and ethene yield are 50 and 42%, respectively. Like the behavior of 3.5 wt% LiCl/SZ, ethene and CO_x selectivities show no deactivation. Investigations on 2 wt% LiCl/SZ and 8 wt% LiCl/SZ reveal that 2 wt% LiCl/SZ shows a similar catalytic behavior as that of 3.5 wt% LiCl/SZ, while 8 wt% LiCl/SZ presents the same characteristic as that of 5 wt% LiCl/SZ. All these results seem to suggest that LiCl loading on catalysts is a crucial factor influencing the catalyst performance. Higher LiCl loading will result in a decrease in activity.

3.2. XRD measurements and BET surface area

The BET surface areas of various catalysts ZrO_2, SZ, LiCl/ZrO_2, LiCl/SZ and Li_2ZrO_3 listed in table 1 indicate that sulfated zirconia shows higher surface area than that of calcined ZrO_2. Impregnation of LiCl greatly decreases the surface area of the corresponding support. It is noted that Li/SZ shows lower surface area than that of Li/ZrO_2, unlike the behavior of the support. Li_2ZrO_3 has the lowest surface area. The variation of surface area must be related to the difference in their chemical structure. XRD patterns of the catalysts are shown in figure 5. It is apparent that these catalysts present different XRD profiles. The major phase of ZrO_2 is monoclinic ZrO_2 with little tetragonal phase, while the two types of crystallites are coexistent in SZ. It is well known that sulfation of zirconia inhibits the sintering and transformation of ZrO_2 from amorphous to monoclinic phase [9,10]. That is the reason that sulfated zirconia exhibits the higher surface area. Surprisingly, the peaks for LiCl were not identified in the LiCl-added samples. This is probably due to the lower amount in amorphous phase or well dispersion of LiCl in the catalysts. However, a small amount of Li_2ZrO_3 was found to be present. The intensities of the Li_2ZrO_3 peaks are weaker on LiCl/ZrO_2. Interestingly, it is found that no tetragonal ZrO_2 existed on the LiCl/SZ sample. The XRD pattern of the Li_2CO_3/SZ sample also shows the presence of only monoclinic ZrO_2 in the catalyst. This suggests that Li promotes the transformation of tetragonal ZrO_2 to monoclinic phase. Srinivasan et al. [11] studied the phase transformations of zirconia and found that the surface sites that adsorb oxygen at low temperatures are responsible for the phase transformation. The incorporation of sulfate covers these sites and inhibits the transformation of tetragonal ZrO_2 to monoclinic ZrO_2. Therefore, it is deduced that lithium additives must cover those surface sites of SZ supports and promote the tetragonal → monoclinic transformation on LiCl/SZ or Li_2CO_3/SZ samples.

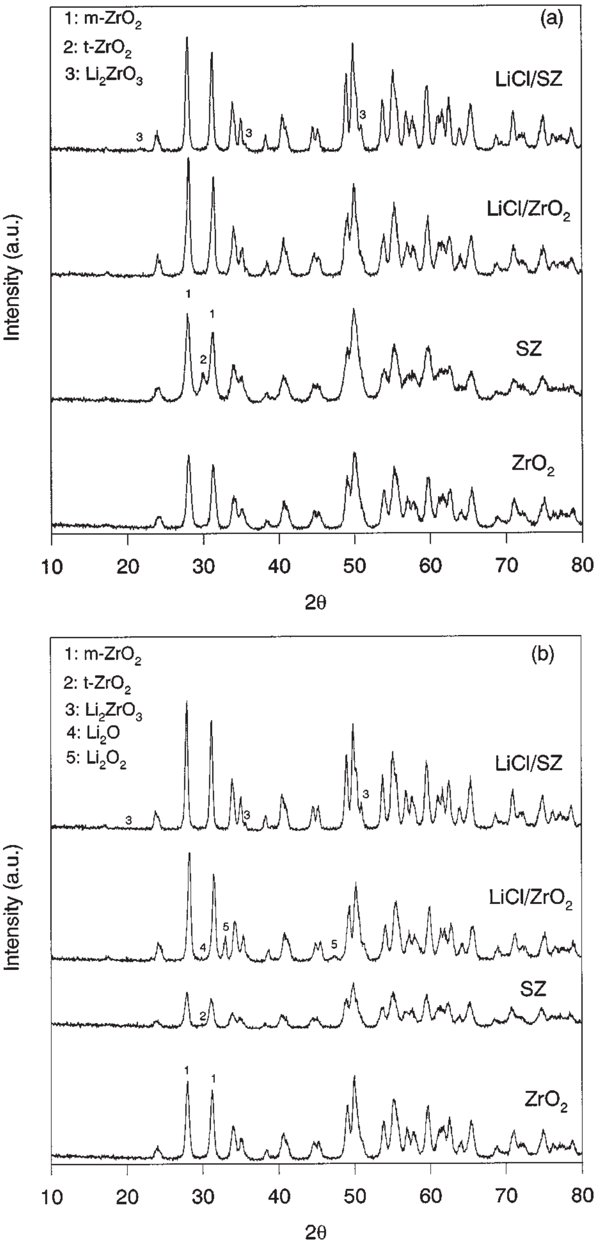

Figure 5. XRD patterns of the fresh (a) and used (b) supports and Li catalysts.

The phases of the used catalysts were also determined by XRD measurements and their XRD profiles are presented in figure 5. It is seen that no phase transformations occurred for ZrO_2 and LiCl/SZ. For SZ, there must be a transformation of tetragonal ZrO_2 to monoclinic ZrO_2 because the peaks of tetragonal ZrO_2 were reduced compared to those of the fresh catalyst. The occurrence of transformation is probably due to the higher reaction temperature. New phases of Li_2O and Li_2O_2 were formed on Li/ZrO_2. This is probably the reason for the lower catalytic activity of LiCl/ZrO_2 than that of LiCl/SZ.

BET measurements indicate that various LiCl/SZ catalysts with different Li loading have a similar surface area. However, their chemical structures show some difference. The XRD patterns of those catalysts are shown in figure 6. It is seen that 2–5 wt% LiCl/SZ catalysts present similar XRD profiles. The crystalline lines on these catalysts represent the presence of monoclinic ZrO_2 and Li_2ZrO_3. The

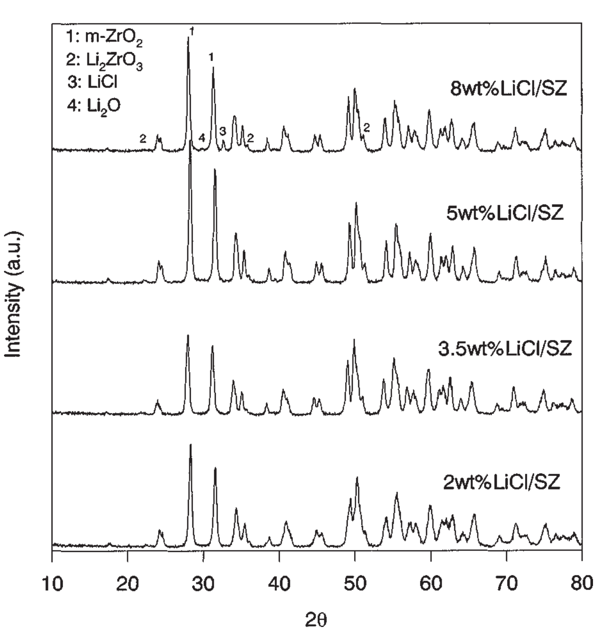

Figure 6. XRD patterns of the various LiCl/SZ catalysts.

peak intensities of Li_2ZrO_3 gradually increase with increasing LiCl loading on the catalysts. For 8 wt% LiCl/SZ, new lines assigned to crystallites LiCl and Li_2O were found. However, the intensities of the Li_2ZrO_3 peaks decrease. This indicates the decomposition of some Li_2ZrO_3 crystallites to Li_2O.

4. Discussion

It is well known that zirconia has a moderate strength of acid and base sites as well as reducing and oxidizing properties [12]. This characteristic makes zirconia act as a catalyst activating gas oxygen to produce oxygen species to react with hydrocarbons. Sulfation of zirconia produces a superacid which is usually used to activate hydrocarbons at lower temperatures. In this investigation, it has been found that zirconia and sulfated zirconia exhibit catalytic activities in ODH of ethane and sulfated zirconia shows higher ethane conversion. The difference in catalytic activity may be due to the different surface chemical properties, surface area and crystallites. BET surface area and XRD results indicate that SZ possesses higher surface area and consists of two types of crystallites (monoclinic and tetragonal ZrO_2), while only one major phase of monoclinic ZrO_2 is present in ZrO_2. Due to the stability of monoclinic ZrO_2, the lattice oxygen is less mobile and active to produce surface species which is important for the activation of ethane. We have conducted temperature-programmed reduction experiments on ZrO_2 and SZ and found that no reduction peak occurs on ZrO_2, while one strong peak appears between 520 and 650 °C on SZ. Further characterization on surface properties is needed to clarify the different activities of ZrO_2 and SZ. For LiCl-promoted catalysts, XRD results demonstrate that ZrO_2 and Li_2ZrO_3 are coexistent. It has been shown that ZrO_2 is the active sites for the reaction. However, Li_2ZrO_3 exhibits less activity for ethane ODH. Thus, it is deduced that the increase in activity of LiCl-added catalysts is due to the synergistic effect of ZrO_2 and Li_2ZrO_3 and the difference in ethane conversion over LiCl/ZrO_2 and LiCl/SZ can be attributed to the ratio of Li_2ZrO_3 and ZrO_2. Of course, it cannot be excluded the effect of surface modification induced by sulfation. Several researches have shown that multiphases in catalysts contribute to the activity of ethane oxidative dehydrogenation in the V–Mg–O system [1,13,14].

It has been reported that Li-doped catalysts are very selective to ethene in ethane ODH because of the increase of active sites for dehydrogenation [4,15]. In this investigation, it has been found that lithium additives increase the ethene selectivity. However, Li/SZ catalysts show different catalytic activities and ethene selectivities depending on their lithium precursors. Sugiyama et al. [16] reported the influence of zirconia preparation on the selectivity for oxidative coupling of methane. They believed that the addition of lithium may affect the formation of methyl radicals. Our investigations of alkali metals and their precursors in tungstated zirconia catalysts in the oxidative coupling of methane also showed different effects of lithium precursors on catalytic activity [17].

Conway and Lunsford [4] found that 5 g Li^+–MgO–Cl^- could produce a C_2H_6 conversion of 75–79% at a C_2H_4 selectivity of 70% with 58% ethene yield at 650 °C under a flow rate of 60 ml/min. Ji et al. [15] also obtained 60% ethane conversion with 75% ethene selectivity, giving 45% ethene yield over Li/La/CaO catalysts at 650 °C. In this investigation, 70% ethene selectivity at 98% ethane conversion with an ethene yield of 68% at 650 °C can be achieved over Li–sulfated zirconia, which is better than those above results.

For the LiCl/ZrO_2 and LiCl/SZ systems in this work, it has been found that the doped Li ions reacted with the support to produce Li_2ZrO_3 crystallites, which exhibit higher selectivity to ethene. For those catalysts chlorine ions can also play an important role for the ethene selectivity. Burch et al. [18] have studied some chloride-promoted oxide catalysts and suggested that the presence of Cl^- ions on the catalyst surface can eliminate the sites for total oxidation and create new sites for the dehydrogenation of ethane to ethene. Wang et al. [19] also proposed that LiCl modified the surface basicity, preventing the decoration of the surface by Li_2CO_3. However, impregnation of more LiCl will cover the active sites for the activation of ethane and oxygen, because LiCl itself is not active for this reaction. Moffat et al. have intensively investigated the effect of introduction of tetrachloromethane into the feedstream for the methane oxidative coupling [20,21] and ethane oxidative dehydrogenation [22,23]. They found that both the conversion and selectivities to the desired products are increased by introduction of tetrachloromethane. The beneficial effects arose from the presence of chloride ions in the interfacial regions of the catalysts. In this investigation, higher activity over LiCl/SZ than over Li_2CO_3/SZ was also observed, which can be ascribed to the role of chlorine. Therefore, it is deduced that added Li and Cl both contribute to the increase in active sites for dehydrogenation. The amount of LiCl on catalysts will affect catalytic activity. The lower catalytic activity of 8 wt% LiCl/SZ can be partly ascribed to poisoning of active sites by LiCl. XRD measurements also show the presence of Li_2O on 8 wt% LiCl/SZ. Li_2O is more liable to react with CO_2, forming Li_2CO_3.

According to the variation of ethene selectivity with temperature over Li/SZ catalysts, it is concluded that ethene is a primary and unstable product, which can be further oxidized to form carbon oxides. Two reaction mechanisms have been proposed for the ODH of ethane [2,24]. One is that ethyl radicals generated by catalysts catalyze the gas-phase conversion of ethane to ethene. The other is that ethoxide species generated by the surface oxygen species decompose into ethene. For the catalysts in this work, we believe that surface-catalyzed reaction by lattice oxygen species dominates the reaction mechanism. At higher temperature, homogeneous gas-phase reaction will contribute to the higher production of ethene because chlorine radicals released from catalysts favor the homogeneous decomposition of ethyl radicals to ethene. We propose the mechanisms as

$$\begin{tikzcd} C_2H_6 + O^*(s) \arrow[r] & C_2H_5(s) + OH(s) \arrow[d, "O^*(s)"] \\ & C_2H_5O \rightarrow C_2H_4 \rightarrow CO, CO_2 \end{tikzcd}$$

$$\begin{tikzcd} C_2H_6 + Cl \arrow[r] & C_2H_5 + HCl \arrow[d, "O_2"] \\ & C_2H_4 \rightarrow CO, CO_2 \end{tikzcd}$$

5. Conclusions

Zirconia and sulfated zirconia exhibit moderate activities for the ethane oxidative dehydrogenation, however, the selectivity over ethene is low. Addition of lithium greatly improves the ethene selectivity. Investigation on the effect of lithium precursor indicates that lithium-chloride-promoted catalysts exhibit best performance in this reaction, increasing the catalytic conversion and ethene selectivity. The loading of lithium on sulfated zirconia also affects the catalytic behavior. 3.5 wt% Li/SZ can give 98% ethane conversion and 70% ethene selectivity at 650 °C. Although LiCl/SZ catalysts show some deactivation, they still can maintain the ethene yield as high as 50% after 24 h testing.

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