Excellent performance of lithium doped sulfated zirconia in oxidative dehydrogenation of ethane

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Sulfated zirconia doped with lithium catalysts are found to be effective for the oxidative dehydrogenation of ethane to ethylene, giving 98% ethane conversion and 70% selectivity towards ethylene as well as 68% ethylene yield at 650 °C.

The selective oxidation of alkanes into their corresponding olefins has been of great interest in recent years. Ethane is an abundant component in natural gas, however, it receives the least attention due to the existing thermal cracking process. Conversion of ethane into ethylene by oxidative dehydrogenation (ODH) has several advantages and been studied over several oxide-based catalysts. Catalysts containing vanadium, molybdate and lithium are found to be effective for this reaction. However, most of these systems are based on alumina, silica, titania and magnesia.[1–4] Little work has concentrated on zirconia, in particular, sulfated zirconia based catalysts. Sulfated zirconia as a super acid solid is known as a very active catalyst for the conversion of small hydrocarbons.[5,6] One of the authors has discovered the excellent performance of Li-doped sulfated zirconia in the oxidative coupling of methane (OCM).[7] The oxidative coupling of methane to C_2-hydrocarbons is inevitably accompanied by the concurrent conversion of ethane to ethylene. Here we report the results of sulfated zirconia based catalysts for the oxidative dehydrogenation of ethane into ethylene.

The zirconia sample was prepared by two steps.[7] The resultant ZrO_2 was then used to prepare sulfated zirconia (SZ) by wetness impregnation using ammonium sulfate, and then calcined at 700 °C for 3 h with a corresponding anion content of 6 wt%. After this, zirconia samples were impregnated with lithium chloride, and calcined at 700 °C for 3 h. The loading of lithium was varied between 2 and 8 wt%. A series of Li-doped sulfacted zirconia (SZ) catalysts were also prepared using different Li precursor compounds at 5 wt% Li content by wetness impregnation as described above. The catalytic tests were carried out in a fixed-bed vertical-flow reactor constructed from a high-purity alumina tube (id = 6 mm) packed with 1.0 g catalyst samples and 2 g quartz sand and mounted inside a tube furnace. The feed, consisting of 10% ethane, 10% oxygen and 80% nitrogen, was introduced into the reactor at a flow rate of 60 ml min^{-1}. The reactants and products were analysed using a gas chromatography (GC-8A) equipped with a Porapak Q column using flame ionisation detector (FID) for hydrocarbons and a 5Å molecular sieve column for CO, CO_2, CH_4, O_2, N_2, and H_2 using thermal conductivity detector (TCD). Before catalyst testing, an empty tube loaded with only quartz sand was evaluated for the oxidative dehydrogenation of ethane under various conditions. It is found that the homogeneous contribution was negligible since ethane conversion was $<2\%$ at 650 °C.

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 Li_2ZrO_3 catalyst. It is found that the main products of ethane oxidative dehydrogenation are C_2H_4, CO and CO_2 with lower amounts of other products such as CH_4, EtOH, and C_3H_6. Ethane conversion increases with the increasing temperature over all catalysts, however, ethylene selectivity exhibits varying patterns with temperature depending on catalyst. For zirconia, sulfated zirconia and Li/ZrO_2, ethylene selectivity increases with temperature.

However, a decreasing trend of ethylene selectivity is observed on Li/SZ at 600–650 °C. Li_2ZrO_3 shows similar ethylene selectivity at the same temperature range. For zirconia and sulfated zirconia, ethane conversions are $>60\%$ with ethylene selectivity of *ca.* 30% at 650 °C. However, sulfated zirconia exhibits slightly higher catalytic activity and selectivity towards ethylene. Doped lithium chloride on supports remarkably improves ethane conversion and selectivity to

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

			Conversion (%)		Selectivity (%)				Yield (%)
Catalyst	S_{BET}/m^2 g^{-1}	T/°C	C_2H_6	O_2	C_2H_4	CO	CO_2	CH_4	C_2H_4
Quartz sand		600	0.2	0.01	97.8			2.2	0.20
		620	0.4	0.4	98.0			2.0	0.39
		650	2.0	2.4	97.7			2.3	1.95
ZrO_2	21.2	600	51.6	100	10.8	24.5	64.4	0.3	5.6
		620	55.4	100	15.0	24.0	60.2	0.8	8.3
		650	65.9	100	29.2	19.2	49.2	1.7	19.2
SZ	72.5	600	42.3	69.7	16.6	38.6	42.6	2.2	7.0
		620	53.8	86.3	18.0	35.6	43.9	2.5	9.6
		650	70.4	100	30.8	18.8	47.3	3.1	21.7
LiCl/ZrO_2	4.6	600	48.8	69.9	54.6	7.3	33.7	0.6	26.6
		620	66.5	83.0	58.3	6.0	28.4	0.8	38.8
		650	87.2	95.3	60.1	9.3	21.8	1.4	52.4
LiCl/SZ	2.0	600	62.4	50.2	82.5	5.4	8.5	0.5	51.5
		620	83.7	69.5	79.5	6.4	10.1	0.6	66.5
		650	97.6	96.3	69.8	11.9	14.3	1.7	68.1
Li_2ZrO_3	<1	600	5.9	6.0	85.7	13.8	0	0.5	5.0
		620	8.3	8.2	86.4	12.9	0	0.7	7.2
		650	20.3	15.1	83.3	8.0	8.0	0.7	16.9

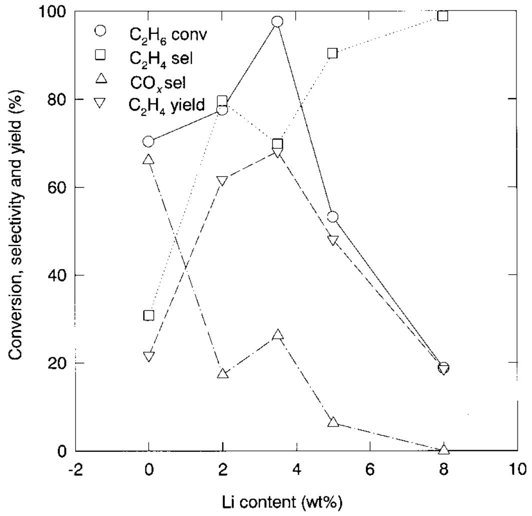

Fig. 1 Effect of Li content in the LiCl/SZ system on catalytic activity.

ethylene. For LiCl/ZrO_2, ethane conversion is enhanced to 87% and ethylene selectivity is increased to > 60%. Similarly, ethane conversion and ethylene selectivity over LiCl/SZ are also significantly improved with 70% selectivity at 98% conversion, giving 68% ethylene yield. LiCl/SZ also exhibits higher ethylene selectivity than Li/ZrO_2, suggesting that sulfation of zirconia modifies the surface properties and could promote ethylene selectivity. It has been found that Li/SZ shows better catalytic performance than Li/ZrO_2 in OCM reaction.[7] Another catalyst, Li_2ZrO_3, shows the lowest catalytic activity, but the highest ethylene selectivity and the ethylene yield is lower than that over the two supports (ZrO_2 and SZ). Several researchers have reported that Li-doped catalysts are much more selective to ethylene in ethane ODH because of the increase of in number of active sites for dehydrogenation.[9,10]

Conway and Lunsford[8] 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% ethylene yield at 650 °C under a flow rate of 60 ml min^{-1}. Ji *et al.*[9] also obtained 60% ethane conversion with 75% ethylene selectivity, giving 45% ethylene yield over Li/La/CaO catalysts at 650 °C. Therefore, the values obtained in this work are much better than the above results.

From Table 1, it can be seen that the catalytic activity is not dependent on the surface area. XRD measurements indicate that two phases (monoclinic and tetragonal ZrO_2) coexist in sulfated zirconia while monoclinic ZrO_2 with a trace of tetragonal ZrO_2 is present in ZrO_2. Li/ZrO_2 and Li/SZ catalysts consist of monoclinic ZrO_2 and a fraction of Li_2ZrO_3 crystallites. The peak intensities for Li_2ZrO_3 are higher for Li/SZ, suggesting that a larger amount of Li_2ZrO_3 is present in Li/SZ. Therefore, it is deduced that the synergistic effect of multiphases in the catalyst are responsible for the catalytic activity and selectivity. For Li doped catalyst, chlorine present in catalyst can also play an important role for the higher selectivity over these catalysts. Some researches have revealed that chlorine can promote the decomposition of ethyl radicals to ethylene.[10,11] Further work on catalyst surface characterisation is in progress to elucidate the active sites for the reaction.

The effect of lithium precursor ($LiNO_3$, LiCl, LiF and Li_2CO_3) in sulfated zirconia systems on the catalytic conversion, ethylene selectivity and yield was also studied. It is found that $LiNO_3$ and LiCl doped SZ catalysts exhibit higher ethane conversions, but that $LiNO_3$/SZ shows the lowest ethylene selectivity. The other three lithium doped SZ catalysts show similar ethylene selectivity. In terms of ethylene yields, LiCl doped sulfated zirconia catalyst generally gives the highest values; the overall order is: LiCl/SZ > $LiNO_3$/SZ > LiF/SZ > Li_2CO_3/SZ.

It is also found that lithium content affects the catalyst performance. The dependence of activity, selectivity and yield of LiCl/SZ catalysts with different lithium content at 650 °C is shown in Fig. 1. It can be seen that ethylene selectivity is enhanced over all Li-doped SZ catalysts. However, the ethane conversion and ethylene yield depend on lithium content. A maximum value can be attained over 3.5 wt% Li/SZ.

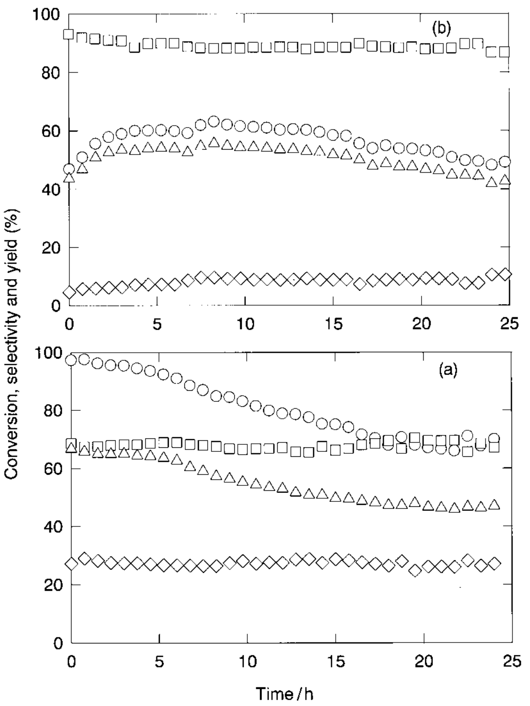

Fig. 2 Catalytic activity of ethane ODH as a function of time over LiCl/SZ at 650 °C.

Fig. 2 shows the catalytic performance of 3.5 wt% LiCl/SZ and 5 wt% LiCl/SZ catalysts at 650 °C in terms of reaction time. One can see that the two catalysts show different stability behaviour. For 3.5 wt% LiCl/SZ ethane conversion and ethene yield decrease gradually over 15 h and then remains nearly unchanged thereafter. Ethane conversion and ethene yields are reduced from 98 and 68% to 70 and 46%, respectively. Ethene and CO_x selectivities stay at the same level during 24 h of testing. The ethane conversion and ethene yield over 5 wt% LiCl/SZ increases in the first 10 h and then decreases, 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 alteration. Investigations on 2 wt% LiCl/SZ and 8 wt% LiCl/SZ reveal that 2 wt% LiCl/SZ shows similar catalytic behaviour as 3.5 wt% LiCl/SZ while 8 wt% LiCl/SZ presents the same characteristics 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. Too high a LiCl content with result in a decrease in activity.

In summary, sulfation of zirconia promotes selectivity towards ethylene in the oxidative dehydrogenation of ethane. LiCl-doped SZ exhibits not only a high ethane conversion but also high selectivity towards ethylene and also high stability.

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