Performance of metal-oxide-promoted LiCl/sulfated-zirconia catalysts in the ethane oxidative dehydrogenation into ethene

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Received 3 June 1999; accepted 6 August 1999

The effects of some transition- and lanthanide-metal oxides in LiCl/sulfated-zirconia (SZ) catalysts on catalytic behavior in the oxidative dehydrogenation of ethane were investigated. It is found that modification of LiCl/SZ by metal oxides significantly improves the catalytic activity and ethene yield. Among those additives, Ni and Nd oxides show the best promoting effect in terms of ethane conversion and ethene yield. 93% ethane conversion with 83% selectivity to ethene has been achieved over the Nd_2O_3–LiCl/SZ catalyst at 650 °C. In addition, those oxide-promoted LiCl/SZ catalysts are also found to exhibit a longer stability in catalytic performance. Metal-oxide additives change the chemical structure and surface redox properties, which accounts for the enhancement of activity.

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

1. Introduction

The oxidative dehydrogenation of ethane (ODE) to ethene being an alternative of the highly endothermic thermal pyrolysis of ethane has attracted much attention in recent years. So far, a great deal of efforts have been made to seek more effective catalysts, especially those showing high selectivity to ethene and good stability for this approach. Alkali-metal and alkaline-earth-metal oxides supported on transition-metal oxides and rare-earth-metal oxides systems and other catalytic materials have been investigated for this reaction in the past decade [1–7]. Li/MgO is perhaps the most effective system and has been widely studied for ODH of ethane. Wang et al. [8] have reported that they obtained 75% ethane conversion and 77% ethene selectivity over a Li^+–MgO–Cl^- catalyst at 620 °C after 50 h on stream.

It has been believed that promoters or dopants in a simple catalyst system will greatly affect the catalytic activity. Conway et al. [9] reported that addition of SnO_2, La_2O_3, Nd_2O_3 or Dy_2O_3 to a Li^+–MgO–Cl^- catalyst significantly improved the activity for the ODH of ethane. The reaction temperature could be lowered without changing the catalytic performance. For example, over a Dy_2O_3/Li/MgO catalyst 75% conversion of ethane with 76% selectivity to ethene was achieved at 570 °C after 25 h on stream. Swaan et al. [10] studied the effects of some oxide additives in Li/MgO on catalytic behaviors in the oxidative dehydrogenation of ethane and oxidative coupling of methane and found that those oxides gave the similar effects for both reactions. However, catalytic activity depended on the nature of dopants. Some dopants exhibited a positive effect on catalytic activity, some showed a negative effect. Ji et al. [11] investigated the influence of Fe, Co and Ni oxides on the behavior of a Li/CaO catalyst in the ODH of ethane. They reported that all Fe, Co and Ni oxides promoted the reactant conversion. However, the ethene selectivity varied. The NiO-promoted catalyst showed higher ethene selectivity while the other two metal oxides reduced the ethene selectivity.

Recently, we have found that Li supported on sulfated-zirconia catalysts exhibited excellent performances in the oxidative coupling of methane and oxidative dehydrogenations of ethane and propane [12–14]. In this work, we report our further investigations on the effect of some oxide additives in LiCl/SZ catalysts on the catalytic activity in the ethane oxidative dehydrogenation.

2. Experimental

Sulfated zirconia (SZ) was prepared by a two-step method. Firstly, $Zr(OH)_2$ was precipitated from a $ZrO(NO_3)_2$ (Wako Chemicals) 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. Then the resultant ZrO_2 samples were impregnated with $(NH_4)_2SO_4$ at an appropriate concentration to reach 6 wt% sulfate content, dried at 105 °C and calcined at 700 °C for 3 h again. The catalysts were prepared by a co-impregnation method on the sulfated-zirconia support. Metal nitrate salts ($Ni(NO_3)_2$, $La(NO_3)_3$, $Ce(NO_3)_3$, $Nd(NO_3)_3$, $Sm(NO_3)_3$ and $Eu(NO_3)_3$), obtained from Wako Chemicals, and LiCl (Wako Chemicals) were dissolved into water and mixed with SZ powder, followed by evaporation. For the vanadium-promoted catalyst, ammonium vanadate (NH_4VO_3) was used. The pastes were dried at 105 °C and calcined at 700 °C for 3 h. The loadings of metal oxides and Li were all kept at 5 wt%.

The surface areas of the support and catalysts were measured by nitrogen adsorption at $-196\,^{\circ}$C according to the BET method on a Micromeritics volumetric equipment provided by Shimadzu. The phase compositions of the catalysts were determined by X-ray diffraction (XRD) on a Philips PW 1800 X-ray diffractometer at 40 kV and 40 mA. The radiation source was Cu $K\alpha$ with a Ni filter. The temperature-programmed reduction (TPR) experiments were conducted in a fixed-bed reactor. 0.5 g samples were loaded and heat-treated under Ar gas flow of 30 ml/min to 700 °C at a heating rate of 5 °C/min and further treated at the same temperature for 30 min. Then the temperature was reduced to the ambient temperature under the same gas flow. After treatment, 10%H_2/Ar flow with a flow rate of 30 ml/min was passed through the reactor and a heating program was started to increase the temperature to 700 °C again at a heating rate of 3 °C/min. The concentrations of H_2 were determined by a GC equipped with a TCD.

The catalytic reactions were carried out in a high purity alumina reactor under atmospheric pressure between 500 and 650 °C. The reactor was loaded with 1 g catalysts and 2 g quartz sand. The gas mixture consisted of ethane, oxygen and nitrogen at the ratio of 1 : 1 : 8 with a flow rate of 60 ml/min. The reactant and product concentrations were analyzed by two on-line gas chromatographs (Shimadzu GC-8A) equipped with a FID and a TCD, respectively. The homogeneous contribution was tested with the quartz sand loaded in the reactor. These runs showed less than 2% ethane conversion at 650 °C. In addition, the carbon balances in all runs were also checked. In all runs, a carbon balance of $100 \pm 5\%$ could be obtained.

3. Results and discussion

The catalytic activities and product distributions of ODE over the unpromoted and promoted LiCl/SZ catalysts at 650 °C are presented in table 1. It is seen that LiCl/SZ is a highly active and selective catalyst, giving 53% ethane conversion and 90% ethene selectivity. Addition of metal oxides reduces the surface areas of the promoted catalysts, however, the ethane conversions are remarkably improved. Oxygen conversion is generally higher over promoted catalysts except for EuLi/SZ. This suggests that catalytic activity does not depend on the surface area, but on the surface chemical properties of catalysts. The different kinds of promoters can modify the surface properties and thus affect the adsorption of oxygen as well as the nature of surface oxygen species. Although the selectivity to ethene is reduced somewhat over all promoted catalysts, it can still be maintained at a high level between 74 and 89%.

For the transition-metal oxides (Ni and V), NiLi/SZ exhibits better catalytic activities with higher values in ethane and oxygen conversions as well as ethene yield. For lanthanide promoters, ethene selectivity is similar for all catalysts, however, ethane conversion shows quite different patterns. One can see that addition of Nd_2O_3 produces the best results in ethane conversion and ethene yield. Ethane conversion is achieved at 97%, the highest among the catalysts prepared, with 84% ethene selectivity, giving 82% ethene yield. Based on the ethene yield, the catalyst activity follows the order NdLi/SZ > NiLi/SZ > LaLi/SZ > SmLi/SZ > CeLi/SZ > VLi/SZ > EuLi/SZ > LiCl/SZ.

Conway et al. [9] studied the promoting effect of some metal oxides (SnO_2, La_2O_3, Nd_2O_3 and Dy_2O_3) in a Li^+–MgO–Cl^- system for the oxidative dehydrogenation of ethane and found that addition of these promoters, in particular the lanthanide oxides, increased the activity without a significant decrease in ethene selectivity. The increase in surface area was partially responsible for the enhancement of catalytic activity. Their observation is different from the results in this investigation. However, chemical modification would be more important for the improvement in catalytic behavior. Swaan et al. [10] studied the effect of some oxide dopants in Li/MgO on catalytic behavior in the oxidative dehydrogenation of ethane and found that catalytic activity varied with the nature of dopants. Addition of cobalt oxide gave an improvement in activity. The addition of cerium and lanthanum had no effect upon the catalyst performance while Sn, Nb, Ti, B and P additives depressed both activity and ethene selectivity. Ji et al. [11] investigated the effect of Fe, Co and Ni oxides on the behavior of Li/CaO catalysts in the ODH of ethane. They reported that Fe, Co and Ni improved the activity. The Ni-promoted catalyst showed higher ethene selectivity, while the other two elements decreased the selectivity. The change of the structure increased the selective oxidation sites, resulting in the enhancement of activity.

Table 1
Catalytic activities of various catalysts in ODE at 650 °C.

Catalyst	S_{BET} (m^2/g)	Conversion (%)		Selectivity (%)				C_2H_4 yield (%)
		C_2H_6	O_2	C_2H_4	CH_4	CO	CO_2	
LiCl/SZ	4.2	53.2	41.8	90.4	0.8	1.5	4.8	48.1
NiLi/SZ	1.4	93.2	86.9	79.1	1.3	7.9	10.0	73.7
VLi/SZ	3.0	66.8	48.3	87.4	0.4	1.8	8.2	58.4
LaLi/SZ	2.3	77.9	83.9	82.2	0.7	3.1	7.2	64.0
CeLi/SZ	1.4	68.6	58.6	87.2	0.5	2.5	6.8	59.9
NdLi/SZ	2.4	97.9	79.4	84.1	0.7	4.0	9.2	82.4
SmLi/SZ	1.8	71.5	68.3	84.4	0.6	3.4	7.1	60.3
EuLi/SZ	1.5	62.9	31.1	89.4	0.4	3.2	4.9	56.2

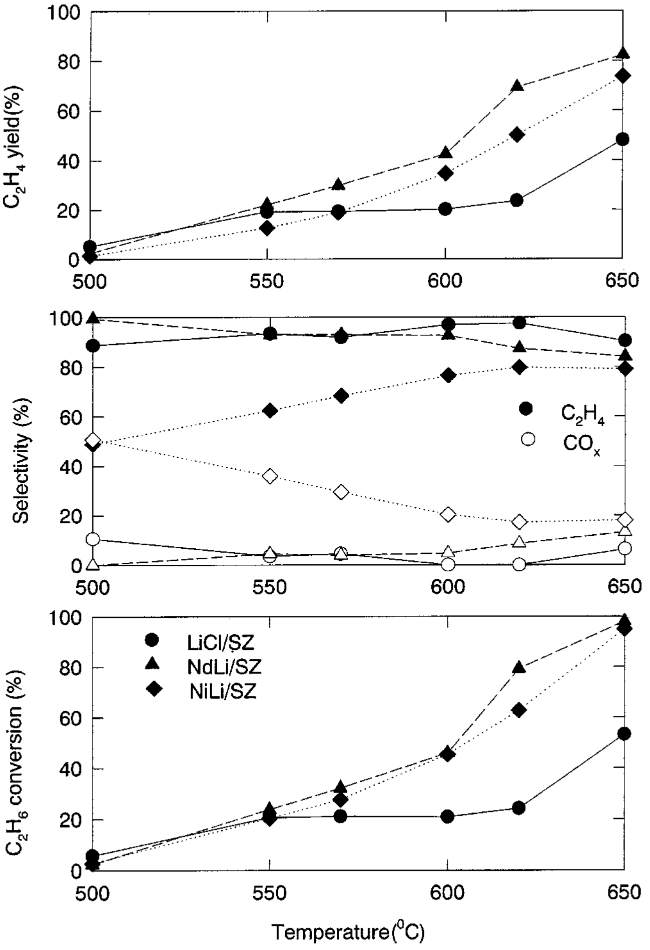

Figure 1. Effect of temperature on catalytic behavior of unpromoted and promoted LiCl/SZ catalysts. Reaction conditions: 1 g catalyst, $F = 60$ ml/min, $C_2H_6 : O_2 : N_2 = 1 : 1 : 8$.

The variation of catalytic activity with the reaction temperature on unpromoted, Ni- and Nd-promoted LiCl/SZ catalysts is shown in figure 1. It can be seen that ethane conversion increases with the increasing reaction temperature. However, ethene selectivity exhibits different patterns. Ni- and Nd-promoted LiCl/SZ catalysts show much similar ethane conversions at all temperatures. For LiCl/SZ and NiLi/SZ catalysts, ethene selectivity generally increases as the temperature increases up to 620 °C. After that the selectivity decreases somewhat. In contrast, ethene selectivity decreases with the increasing temperature over NdLi/SZ catalyst. This suggests that the relative contribution of homogeneous and heterogeneous reactions from those catalysts may be different. For NdLi/SZ, the surface reactions producing ethoxide species and decomposition into ethene play a more important role, while for LiCl/SZ and NiLi/SZ, a homogeneous gas-phase reaction induced by chlorine radicals released from the catalysts will contribute to the higher production of ethene. Martin et al. [15] reported that selectivity to ethene increases with increasing temperature for ODH of ethane over the Li/MgO catalyst, similar to the results of the LiCl/SZ and NiLi/SZ catalysts in this investigation. Au et al. [16] also reported the similar phenomenon over a $BaCl_2/Ho_2O_3$ catalyst. The increase of selectivity to ethene with increasing temperature is probably due to the fact that the formed ethyl radical at high temperature desorbed and formed ethene in the gas phase via reaction with oxygen. Chlorine radicals favor the homogeneous decomposition of ethyl radicals to ethene [7]. At 650 °C, ethene selectivity decreased over NiLi/SZ and LiCl/SZ is probably due to the homogeneous over-oxidation of ethene.

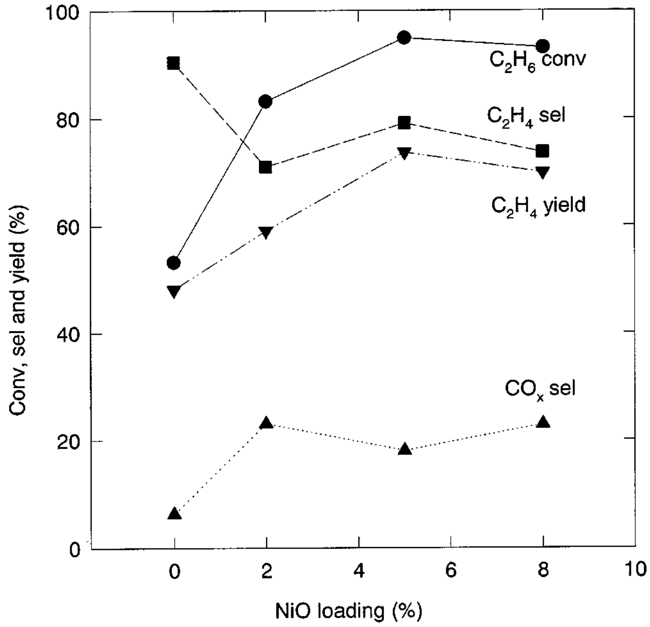

Figure 2. Effect of NiO loading in NiLi/SZ on catalytic activity. Reaction conditions: 1 g catalyst, $F = 60$ ml/min, $C_2H_6 : O_2 : N_2 = 1 : 1 : 8$, $T = 650$ °C.

The influence of metal-oxide content on catalytic activity was investigated over NiLi/SZ catalysts and the results are shown in figure 2. It is seen that ethane conversion increases with the increasing NiO content and reaches the highest value at 5 wt% NiO loading. Although the ethene selectivity decreases over all NiLi/SZ catalysts no matter what the NiO loading is, ethene yields still show higher values than that of unpromoted LiCl/SZ. From the viewpoint of ethene yield, 5 wt% NiO will be the optimal content at which a maximum yield can be achieved.

The catalytic performance of unpromoted, Ni- and Nd-promoted LiCl/SZ catalysts as a function of time at 650 °C was further investigated (figure 3). It is shown that ethane conversion and ethene yield over the 5 wt% LiCl/SZ increase in the first 10 h and then show a decreasing trend, however, the deactivation rate is slow. After 25 h testing, ethane conversion and ethene yield are 50 and 42%, respectively. For the other two promoted catalysts, ethane conversions also display an increasing trend in the first 10 h, as the behavior of the unpromoted LiCl/SZ. After that activities can be maintained at the same level until 20 h testing. Thereafter a deactivation behavior is observed. However, the deactivation rates are still lower than that over the unpromoted catalyst. Ethane conversion and ethene yield over NdLi/SZ after 25 h are 93 and 75%, respectively, while they

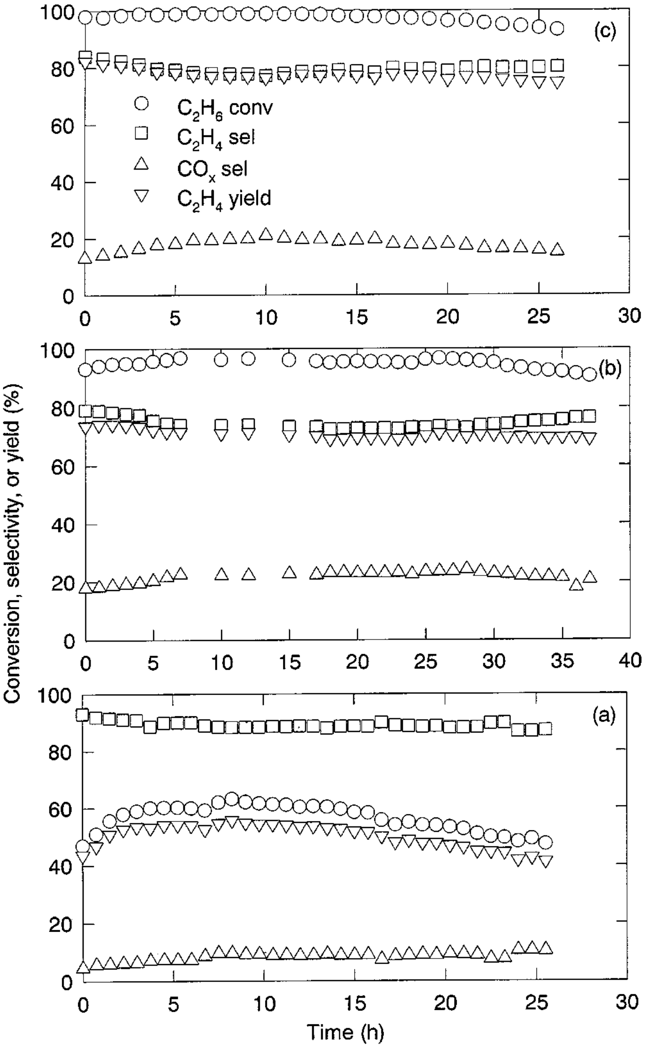

Figure 3. Stability performance of unpromoted and promoted LiCl/SZ catalysts at 650 °C. Reaction conditions: 1 g catalyst, $F = 60$ ml/min, $C_2H_6 : O_2 : N_2 = 1 : 1 : 8$.

are 91 and 69%, respectively, over NiLi/SZ after about 40 h. These results indicate that the promoted catalysts exhibit a longer stability in ODE.

The chemical structure of unpromoted, Ni- and Nd-promoted LiCl/SZ catalysts were determined by XRD and their patterns are shown in figure 4. One can see that two phases are present in the LiCl/SZ catalyst, monoclinic ZrO_2 and Li_2ZrO_3. However, no LiCl peaks were identified in the XRD profiles. This is probably due to the lower amount in amorphous phase or good dispersion of LiCl in catalysts. For Ni- and Nd-promoted catalysts, apart from m-ZrO_2 and Li_2ZrO_3, NiO and Nd_2O_3 are found present in each promoted catalyst, respectively. It is noted that the diffraction peaks of Li_2ZrO_3 show lower intensity on the NdLi/SZ catalyst, suggesting a smaller amount of Li_2ZrO_3 produced on this catalyst.

Figure 5 illustrates the TPR profiles of those three catalysts. As seen from the figure, one reduction process occurs on LiCl/SZ and NdLi/SZ catalysts with varying temperature and intensity. The reduction of LiCl/SZ begins from 600 °C while the reduction occurs earlier from 500 °C on NdLi/SZ and the reduction extent is much higher. This process is probably due to the reduction of Li_2ZrO_3 and Nd_2O_3. XRD measurements of the reacted catalysts show the presence of Li_2O and Li_2O_2 on some catalysts. For NiLi/SZ, two reduction processes can be observed. The first one occurs between 300 and 500 °C centered at 400 °C, which can be attributed to NiO reduction. The other reduction is after 600 °C, similar to that of the other two catalysts

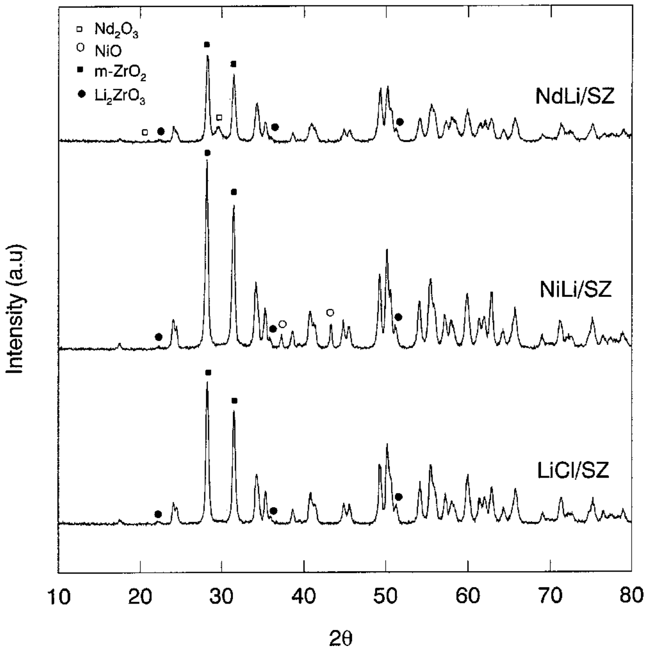

Figure 4. XRD patterns of unpromoted, Ni- and Nd-promoted LiCl/SZ catalysts.

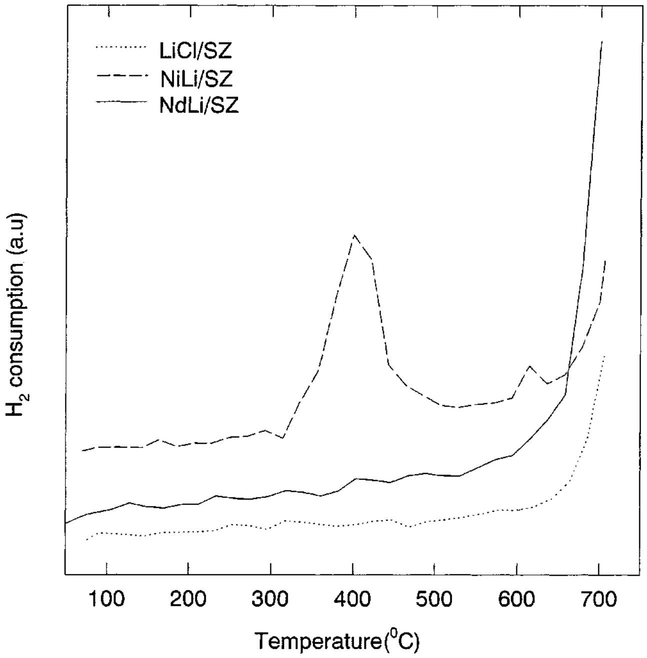

Figure 5. TPR profiles of unpromoted, Ni- and Nd-promoted LiCl/SZ catalysts.

and the strength is also similar to that on the unpromoted LiCl/SZ.

It has been believed that the oxidative dehydrogenation of ethane proceeds in a redox process on the catalyst surface via ethane and surface oxygen species. The distribution of oxygen species generated from O_2 adsorption depends on the properties of the catalyst and can determine the distribution of the products. Among the oxygen species, O^- is responsible for the activation and selective oxidation of hydrocarbons, while dioxygen species are more capable of causing complete oxidation [17]. The acid–base and redox properties of catalysts are important factors influencing the oxygen species production. Addition of some promoters will definitely modify those properties. XRD measurements show that no solid reaction occurred between promoters and the support (ZrO_2) on those modified catalysts. The new phases formed are the metal oxides, which are believed to exhibit redox property. TPR profiles have shown that unpromoted, Ni- and Nd-promoted LiCl/SZ catalysts do exhibit varying reducibility and reduction strength. Addition of metal oxides (NiO and Nd_2O_3) increases the extent of reduction of the promoted catalysts. Schuurman et al. [18] have investigated the oxidative dehydrogenation of ethane over Ni-, Co- and Fe-oxide catalysts and observed that Ni catalysts could show activity at lower temperatures while having high and constant ethene selectivity. Using the TAP technique, they found that the oxygen species involved in the reaction mechanism over Ni catalysts is not the gas-phase dioxygen molecule. O^- would abstract hydrogen atoms from the ethane to give ethene. It is well known that vanadium oxides exhibit a significant catalytic activity in the oxidative dehydrogenation of alkanes [19,20]. The rare-earth-metal oxides are also found active for dehydrogenation of ethane [5,6,21,22] and their based halide catalysts can produce surface oxygen defects and O_2^- species, responsible for dehydrogenation [23,24]. From table 1, it has been shown that oxygen conversion on promoted catalysts is higher, suggesting an easiness of oxygen activation. Therefore, it can been deduced that addition of promoter induces a synergistic effect, resulting in the increases in the active sites for the activation of ethane and oxygen and enhancement of the reaction between ethane and oxygen species and thus higher ethane conversion, but lower ethene selectivity over promoted LiCl/SZ catalysts. Further research on catalyst surface properties is being conducted.

The difference in activity of unpromoted and oxides-promoted catalysts may also be attributed to the different chemical phases existing in the catalysts. It has been found that Li_2ZrO_3 shows much lower activity in the oxidative dehydrogenation of ethane or propane than do zirconia and sulfated zirconia [13,14]. XRD measurements show that more Li_2ZrO_3 particles formed on LiCl/SZ and NiLi/SZ catalysts, which can partly account for the lower ethane conversion over these two catalysts. Further research is being conducted so as to elucidate the reaction mechanisms over those catalysts.

4. Conclusion

LiCl/SZ is a very effective and highly selective catalyst for the oxidative dehydrogenation of ethane. Ethene productivity can be greatly improved by addition of some transition- and lanthanide-metal oxides. Metal oxides will enhance the redox ability of catalyst, resulting in adsorption and activation of oxygen into oxygen species and favoring the selective dehydrogenation of ethane into ethene. Among the oxides tested, Nd_2O_3 is the most promising dopant whose promoted catalyst exhibits the highest ethane conversion and ethene yield.

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