Study of ODE Reaction over Binary Rare Earth Oxyfluoride Sm_2O_3-LaF_3 Catalysts

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The oxidative dehydrogenation of ethane (ODE) reaction has been investigated over Sm_2O_3-LaF_3 and BaF_2 promoted Sm_2O_3-LaF_3 catalysts. Over Sm_2O_3-LaF_3(molar ratio=1:1) and 16.7 mol% BaF_2/Sm_2O_3-LaF_3(molar ratio=1:1) high C_2H_4 selectivities of 89.7% and 83.9% were achieved respectively. XRD and XPS characterizations show the electron donating ability of the catalysts are stronger that corresponding rare earth oxide and fluoride. The addition of BaF_2 can increase the number of the structure defects that may enhance the electron donating ability and increase the surface adsorbed oxygen concentration, thus should be favorable to improving the catalytic performance. However, the higher concentration of surface adsorbed oxygen is unfavorable for the ethene formation.

Recently, several research groups have found that the catalytic properties of metal oxides for the oxidative coupling of methane (OCM) and ODE reaction can be promoted by adding of halides, especially chlorides.[1-3] Lunsford et al. has demonstrated that the addition of chloride ions to Li^+-MgO catalysts significantly improved the catalytic performance for both OCM and ODE reaction.[2,3] But the utilizing of fluorides, which, especially rare earth and alkaline earth fluorides, should be more stable than the corresponding chlorides under the conditions of OCM and ODE reaction, has been seldom studied.[4,5] In this paper, the promoting effects of rare earth and alkaline earth fluorides on Sm_2O_3 and Sm_2O_3-LaF_3 catalysts were reported.

The catalysts were prepared according the same procedure described elsewhere.[4] The catalytic performance were performed under the conditions of $C_2H_6:O_2:N_2=2:1:7$, flow rate 40 ml/min and the reaction temperature 973 K. All data were taken after 4 hours on stream. The results of the reaction are listed in Table 1.

Pure Sm_2O_3 or LaF_3 shows moderate catalytic performance for ODE reaction under the experimental condition. Depending on their relative contents, binary rare earth oxyfluorides Sm_2O_3-LaF_3 are generally active and selective for the ODE reaction. For SL2 catalyst, at 973 K, the ethene selectivity is 89.7%, which is higher than that of SL1 and SL3(Table 1). The addition of BaF_2 significantly improves the catalysts performance, but the promoting effect is different from each other. For the SL2 catalyst, after the addition of BaF_2 the C_2H_6 conversion is improved from 22.1% to 42.0%, meanwhile, the ethene selectivity decreased from 89.7% to 83.9%. While for the BaF_2 doped other catalysts, BSL1 and BSL3, both the ethane conversion and the ethene selectivity are increased as compared with SL1 and SL3. From above results , it can be concluded that seemly the molar ratio of Sm_2O_3 and LaF_3 is an important factor for catalyst which is highly selective to ethene. Equal molar amount of Sm_2O_3 and LaF_3 appears to be favorable for the formation of ethene.

Table 1. The results of Sm_2O_3-LaF_3 & BaF_2/Sm_2O_3-LaF_3 for ODE

No.	Catalysts Composition	Selectivity(%)				Conv.	Yield of
		CH_4	CO	CO_2	C_2H_4	C_2H_6(%)	C_2H_4(%)
S0	Sm_2O_3	2.5	10.3	29.9	57.3	45.2	25.9
L0	LaF_3	2.0	0.0	29.8	68.2	20.9	14.2
SL1	Sm_2O_3/LaF_3(1.:3)[a]	8.2	5.2	25.4	61.2	53.1	32.5
SL2	Sm_2O_3/LaF_3(1:1)	5.1	3.1	2.1	89.7	22.1	19.8
SL3	Sm_2O_3/LaF_3(3:1)	7.9	3.7	25.3	63.1	56.1	35.4
BSL1	BaF_2/SL1 (1:5)	8.3	3.8	26.4	65.9	55.0	36.3
BSL2	BaF_2/SL2 (1:5)	7.3	2.6	6.2	83.9	42.0	35.3
BSL3	BaF_2/SL3 (1:5)	6.1	3.4	22.8	67.7	62.9	42.6

[a] The molar ratio is shown in parenthesis.

XRD measurement results reveal that for the SL1 and SL3 catalysts, several phases such as rhombohedral LaOF, SmOF, cubic Sm_2O_3 coexisted in the bulk, but for the SL2 catalyst, only rhombohedral oxyfluoride phase existed. Because the molar ratio of Sm_2O_3/LaF_3 in SL2 is 1:1, the composition of this phase should be binary rare earth oxyfluoride $Sm_{2/3}La_{1/3}OF$. The formation of the oxyfluorides implies that that partial anions and/or cations exchange and interaction between oxide and fluoride phase might happen. Adding 16.7 mol% BaF_2 into the catalysts, slightly constricted cubic BaF_2 phase appeared in addition to the original phases. This result indicated that the partial anions and/or cations exchange between BaF_2 and the original phases happened and this kind of exchange should increase the number of defect sites, and thus be favorable for the methane and ethane conversion.[4-6] The existence of the structure defects will be discussed in the following XPS results.

XPS measurement were carried out at room temperature. The sample was pressed to wafer under $100 kgf/cm^2$. After heating at 523K for 6 hours, the wafer was transferred to the sample chamber and keeping under the high vacuum ($<1 \times 10^{-10}$ pa) for at least 2 hours before the measurement. The on-line MS shown that there were no water but little CO and CO_2 in the chamber under the measurements. The binding energies of $La3d_{5/2}$ (834.4 ± 0.2 eV) and $Sm3d_{5/2}$ (1082.3 ± 0.2 eV) are almost same in SL1, SL2 and SL3 catalysts. However, these binding energies are 0.5-1.5 eV lower than the standard binding energies of $La3d_{5/2}$(834.92 eV in La_2O_3 and 836.0 eV in LaF_3) and $Sm3d_{5/2}$ (1083.2 eV in Sm_2O_3).[7] This result reveals that the structure defects (F-center and anionic vacancies) exist around the La^{3+} and Sm^{3+} due to ionic substitution such as that of O^{2-} for F^-, and thus the electron denoting ability was increased. Adding 16.7 mol% BaF_2 into SL1, SL2, and SL3 catalysts, the binding energies of $La3d_{5/2}$ and $Sm3d_{5/2}$ are almost as same as the SL catalysts, while the difference (△) between the binding energy of $La3d_{5/2}$ and $La3d_{3/2}$ decreased slightly (see in Table 2.). The reduce of the △ might imply that ligand field surround La^{3+} in BSL-series catalysts is weaker than that of corresponding SL-series catalysts, and might be caused by the existence of more structure defects such as F-center and anionic vacancies in the BSL-series catalysts

The performance of active and selective oxygen species is one of the most important function of the catalysts for partial oxidation. XPS results show that there are two kinds of O_{1s} with

Table 2. XPS results over SL-series and BSL-series catalysts

Catalyst	SL1	SL2	SL3	BSL1	BSL2	BSL3
$O_{adsorb}/O_{lattice}$	1.48	1.16	1.37	1.94	1.26	1.80
Sm3$^+$/La3$^+$	4(2:3)^a	2.0(2:1)	10(6:1)	3.8(2:3)	1.9(2:1)	9.6(6:1)
△ (eV)	17.0	16.8	16.9	16.8	16.6	16.6

^{a}The bulk atom ratio is shown in parenthesis; △ The binding energy difference between $La3d_{5/2}$ and $La3d_{3/2}$.

binding energies at 531.8 eV and 528.9 eV, respectively, on those catalysts. The latter can be assigned to O^{2-} lattice oxygen.[2,8,9] The assignment of the former peak is rather difficult, because both CO_3^{2-} and O_2^{2-} (O^-) ions may show peaks in this region.[8,9] However, the peaks of C1s (289.0 eV) show almost same intensity for all of the six samples, we temporarily assigned the peak at 531.8 eV to the adsorbed oxygen totally in order to get some general informative results. The quantitative results of the oxygen species are listed in Table 2.

Among the unpromoted catalysts of SL1, SL2 and SL3, the atom ratio of $O_{adsorb}/O_{lattice}$ on SL2 (1.16) is smaller than that of SL1(1.48) and SL3(1.37). Adding 16.7 mol% BaF_2 into the catalysts, the atom ratios of $O_{adsorb}/O_{lattice}$ remained in the same order BSL2(1.26) < BSL1(1.94), BSL3(1.80) and all of the promoted catalysts have higher $O_{adsorb}/O_{lattice}$ ratios than the corresponding unpromoted catalysts. In the catalytic evaluation experiments, the ethane conversion sequence is SL2 < SL1, SL3 and BSL2 < BSL1, BSL3, but the ethene selectivity sequence is in the opposite order. From Table 1, it can be also seen that BaF_2 promoted catalysts have better catalytic performance than the corresponding unpromoted catalysts, suggesting that for the same series catalyst (SL1, SL2 and SL3 or BSL1, BSL2 and BSL3) the higher surface adsorption oxygen concentration is favorable for the ethane conversion, but unfavorable for the ethene selectivity. BaF_2 may exchange ions with the other phases such as rhombohedral LaOF and SmOF in SL-series catalysts to produce more structure defects which is favorable for the adsorption and activation of molecular oxygen and improving the catalytic performance, especially activity.

The surface atom ratios of Sm^{3+}/La^{3+} for the six samples are given in Table 2. After the addition of BaF_2 into Sm_2O_3-LaF_3 catalysts, the atom ratios of Sm^{3+}/La^{3+} varied a little. This indicated that there were almost equal opportunities for the exchange of Ba^{2+} with La^{3+} and with Sm^{3+}. Comparing the six catalysts, the molar ratios of Sm^{3+}/La^{3+} is higher than that in bulk except for SL2 and BSL2 in which the atom ratios are closed to the bulk atom ratios. This might be attributed to that the single phase rhombohedral $Sm_{2/3}La_{1/3}OF$ which is a superstructure of fluorite with stoichiometric composition existed in SL2 and BSL2 catalysts, and that Ba^{2+} was well dispersed in $Sm_{2/3}La_{1/3}OF$.

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