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Oxidative dehydrogenation of propane over fluorine promoted rare earth-based catalysts

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Catalysts based on rare earth complexes such as $CeO_2/2CeF_3$, $Sm_2O_3/4CeF_3$, $Nd_2O_3/4CeF_3$ and $Y_2O_3/4CeF_3$ were prepared. These catalysts were active for the oxidative dehydrogenation of propane with very high selectivity to propene. At 500°C and 6000 h^{-1}, using $CeO_2/2CeF_3$ as the catalyst, the conversion of propane was 41.3%, selectivity to propene reached 81.1%, propene yield was 33.5%. XRD results indicated that F^- and O^{2-} were exchanged in the lattices. Raman spectra showed that the O_2^- might be the active oxygen species in propane oxidative dehydrogenation.

Keywords: Propane; propene; oxidative dehydrogenation; rare earth catalyst

1. Introduction

Increasing attention has been focused on the utilization of cheaper feedstocks, such as alkanes in industrial chemistry. Light carbon alkanes which are abundant in natural gas and liquefied petroleum gas have been used to produce alkene or oxygenated organic compounds [1]. The oxidative dehydrogenation (OXD) of alkanes to unsaturated hydrocarbons is a promising route. So far, only a few catalysts have been reported to show reasonable selectivity for this reaction, particularly under conditions of high conversion [2,3]. We report here that rare earth-based catalysts which were composed of oxides of Ce, Sm, Nd or Y and CeF_3 preserved high selectivity at higher conversion.

2. Experimental

(1) The catalysts were prepared separately from the following reagents (all ratios are in mol):

DCE: CeO_2/CeF_3 (1 : 2); DSM: Sm_2O_3/CeF_3 (1 : 4),
DND: Nd_2O_3/CeF_3 (1 : 4); DY: Y_2O_3/CeF_3 (1 : 4).

The above mixtures were crushed and then stirred with deionized water to paste respectively. The pastes were dried at 100°C for 1 h, calcined at 850°C for 2 h, and then crushed to 0.22–0.50 mm particle size. In this way, the catalysts DCE, DSM, DND and DY were prepared.

(2) The catalytic reaction was carried out in a fixed bed reactor using 0.5 ml of catalyst. The feed rate of reactant ($C_3H_8 : N_2 : O_2 = 4 : 11 : 5$) was 50 ml/min. The products were analyzed with gas chromatography.

(3) The XRD measurements of the fresh catalysts were carried out by using Rigaku Rotaflex D/Mac-C system with Cu Kα radiation.

(4) The Raman spectra were recorded by using Jobin Yvon U-1000 Raman spectrometer. The treatment of the samples used in Raman characterization was as follows: the catalyst sample was treated in flowing N_2 at 900°C for 30 min, then cooled to room temperature. Part of the sample was sealed in a glass tube in N_2, for the sample without adsorbed O_2 (background sample). Part of the sample was exposed to O_2 at room temperature, and then flushed with N_2 at room temperature before sealing, to obtain a sample with adsorbed O_2.

3. Results and discussion

Table 1 shows the results of propane OXD over the catalysts at 500°C. The selectivity to propene is very low over the pure oxides. Most of the converted propane was cracked to CH_4, C_2H_4 or completely oxidized to CO and CO_2. The propane conversion was very low over CeF_3 at 500°C. After addition of CeF_3 to CeO_2, Sm_2O_3, ND_2O_3 and Y_2O_3, the selectivity to propene greatly increased. Over the $CeO_2/2CeF_3$ catalyst, the conversion of propane was 41.3%, the selectivity to propene increased to 81.1%. Over the $Nd_2O_3/4CeF_3$ and $Y_2O_3/4CeF_3$ catalyst, the

Table 1

Results of propane oxidative dehydrogenation over rare earth-based catalysts [a]

Catalyst	Conv. of C_3H_8 (%)	Selectivity (%)						Yield of C_3H_6 (%)
		C_3H_6	CH_4	C_2H_6	C_2H_4	CO_2	CO	
CeO_2	86.7	7.9	39.8	3.1	23.9	17.8	7.0	6.85
Sm_2O_3	33.3	6.3	30.2	3.0	19.3	34.1	7.3	2.1
CeF_3	n.a. [b]							
$CeO_2/2CeF_3$	41.3	81.1	3.8	0	10.7	0.8	3.6	33.5
$Sm_2O_3/4CeF_3$	7.5	92.8	0	0	0	7.2	0	6.96
$Nd_2O_3/4CeF_3$	8.8	99.0	0	0	0	1.0	0	8.71
*	32.7	71.3	11.6	0	16.7	2.1	0	23.3
$Y_2O_3/4CeF_3$	9.0	97.0	0	0	0	3.0	0	8.73
*	33.3	65.4	14.2	0	16.3	4.0	0	21.8

[a] Reaction temperature: 500°C (* :520°C), space velocity: 6000/h.

[b] n.a.: no activity.

conversions of propane were 8.8 and 9.0% respectively, and the selectivities to propene were greater than 90%. From table 1, we find that over $CeO_2/2CeF_3$, the yield of propene (33.5%) was much higher than for the other catalysts (6.96% to 8.73%) at 500°C. Table 1 also shows that the increase of the reaction temperature can apparently increase the conversion of propane, but decreases the selectivity to propene. For example, over $Nd_2O_3/4CeF_3$ catalyst, the conversion of propane reached 32.7% at 520°C (only 8.8% at 500°C), and the selectivity to propene was 71.3% (99.0% at 500°C).

XRD results indicated that in $CeO_2/2CeF_3$, only cubic CeO_2 phase was found, but its lattice constant increased a little. This might be caused by CeF_3 melting into the CeO_2 lattice. The $Nd_2O_3/4CeF_3$ catalyst contained cubic CeO_2 and hexagonal NdF_3. In $Y_2O_3/4CeF_3$, cubic CeO_2, orthorhombic YF_3 and a small amount of hexagonal YOF were found. These results showed that in the catalysts $Nd_2O_3/4CeF_3$ and $Y_2O_3/4CeF_3$, F^- and O^{2-} exchanged in the lattice. This kind of exchange would form anion vacancies because one O^{2-} can substitute two F^-. The melting of CeF_3 into CeO_2 changed the lattice constant and the basicity of CeO_2. These affect the oxygen adspecies greatly. It is favourable for the oxidative dehydrogenation of propane.

Raman spectroscopy was used to characterize active oxygen species on the catalysts. Fig. 1 shows the Raman spectra of the $CeO_2/2CeF_3$ catalyst. With no O_2 adsorbed, there is only one band at 944 cm^{-1}, corresponding to M=O vibration in CeO_2. With O_2 adsorbed, a new band appeared at 1166 cm^{-1}, corresponding to O_2^- [4]. The Raman spectrum of the used catalyst was complex, showing four bands at 1030–1085 cm^{-1}, and two bands at 1426 and 1470 cm^{-1}. The last two bands correspond to CO_3^{2-} [4]. This indicated CO_3^{2-} was formed on the catalyst surface in the reaction. The Raman spectra did not show the signals of O^- and O^{2-} on the surface of the O_2 adsorbed sample, only O_2^- was checked. These results apparently showed the activity of $CeO_2/2CeF_3$ catalyst to O_2. The O_2^- might be the active oxygen species in propane OXD.

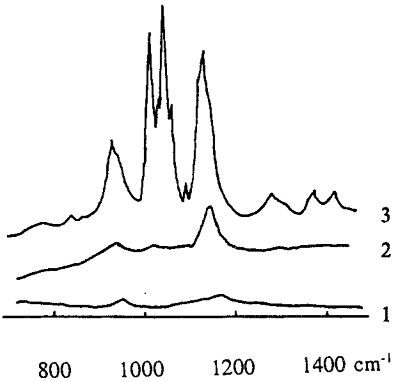

Fig. 1. Raman spectra of catalyst $CeO_2/2CeF_3$. (1) no O_2, (2) O_2 adsorbed, (3) after reaction.

4. Conclusion

The investigation indicated that after CeF_3 addition to CeO_2, Sm_2O_3, Nd_2O_3 or Y_2O_3, the F^- and O^{2-} exchange in the lattice. The "isolation effect" of F^- at the surface for oxygen adspecies and the basicity difference of surface oxygen species affect the OXD of propane, increasing the selectivity to propene.

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