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The activation of O_2 and the oxidative dehydrogenation of C_2H_6 over SmOF catalyst

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The activation of O_2 over SmOF was studied by in situ laser Raman spectrometry and temperature programmed desorption (TPD). When the hydrogen- and helium-treated (1 h for each gas at 973 K) SmOF sample was cooled to 303 K in oxygen, Raman bands which correspond to the existence of O_2^{2-}, O_2^{n-} ($2 > n > 1$), O_2^- and $O_2^{\delta-}$ ($1 > \delta > 0$) species were observed. From 303 to 973 K, there was no O_2 desorption but the Raman bands observed at 303 K reduced in intensity and vanished completely at 973 K, even though the sample was under an atmosphere of oxygen. We suggest that as the sample temperature increased, dioxygen species were converted to mono-oxygen species such as O^- which were undetectable by Raman spectrometry. O_2 desorption occurred above 973 K, giving a TPD-peak at 1095 K. When C_2H_6 was pulsed over the sample pretreated with oxygen and helium at 973 K, C_2H_4 selectivity was 91.8%. We conclude that the mono-oxygen species is responsible for the oxidative dehydrogenation of ethane to ethene.

Keywords: ethane oxidative dehydrogenation; O_2 activation; SmOF; dioxygen species and mono-oxygen species

1. Introduction

Oxygen species have been studied extensively in catalytic processes such as the selective oxidation of hydrocarbons. Since molecular oxygen is a common oxidizing agent, its activation is a vital step to be considered. The distribution of oxygen species generated from O_2 adsorption is determined by the properties of the catalyst used. A catalyst may induce the generation of a particular type of oxygen species and consequently is able to fulfil its specific role in a catalytic reaction. For examples, Wang and Lunsford [1] suggested that in the catalytic oxidation of alkane to alkene, O^- is responsible for the high alkene yield; in the activation of methane over rare earth oxides, Lunsford et al. [2] suggested that the O_2^{2-} species was involved in the process.

As related to the reaction mechanism of ethane oxidative dehydrogenation, Morales and Lunsford [3] suggested that ethane was first dehydrogenated to ethyl radical $C_2H_5\cdot$ which might then react with surface O^- to form $C_2H_5O^-$(s) or desorb and react with gaseous O_2 to form $C_2H_5O_2\cdot$(g). Both $C_2H_5O^-$ and $C_2H_5O_2\cdot$ are precursors for C_2H_4, CO_2, CO and H_2O generation.

In this paper, we attempted to identify the oxygen species which is responsible for C_2H_4 generation in the oxidative dehydrogenation of ethane over SmOF.

2. Experimental

The catalyst SmOF was prepared by mixing Sm_2O_3 (> 97% purity) and SmF_3 (prepared by reacting Sm_2O_3 with HNO_3 in deionized water followed by precipitation with HF solution) in 1 : 1 molar ratio. The mixture was ground to powder which was then extruded (300 kg/cm^2) to pellets. After being calcined in air at 1173 K for 6 h, the pellets were crushed and sieved to 20–40 mesh. XRD examination revealed that the product was rhombohedral SmOF.

In situ laser Raman experiments were performed on a Jobin Yvon U-1000 laser Raman spectrometer. Sample treatment was conducted in a cell which could be heated to a temperature between 298 and 1023 K.

TPD and pulse experiments were carried out using a pulse quartz microreactor (i.d. 3 mm) connected on-line to a GCD (Hewlett G1800A, Porapak Q column) system. The flow rate of the carrier gas helium was 12.0 and 4.5 ml min^{-1} respectively for TPD and pulse experiments. The amount of catalyst used was 0.2000 g.

Oxygen used in the experiments was purified by passing through a column of molecular sieve 5A (to remove CO_2 and H_2O) which was pretreated in helium at 773 K for 4 h. The gases helium and ethane were purified (oxygen level < 5 ppb) by the catalyst 401 (product of Dalian Chemical Physics Institute, PR China).

3. Results and discussion

3.1. *The characterization of oxygen species in SmOF*

After the SmOF sample was heated in H_2 at 973 K for 1 h and then helium purged at the same temperature for another hour, it was cooled from 973 to 303 K in O_2.

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The Raman spectrum showed bands at 668, 984, 1026, 1128, 1184, 1402, and 1460 cm^{-1} within the 600 to 1550 cm^{-1} range (fig. 1, spectrum (a)). As the sample was heated in O_2 stepwise to 473, 573, 673 and 773 K, the intensity of the Raman bands within the 880 to 1550 cm^{-1} region decreased monotonously (spectra (b)–(e)). From 303 to 473 K, there was a gain in intensity for the 668 cm^{-1} band and as the temperature rose higher, the band decreased in intensity. At 773 K, no matter the sample was in oxygen or in helium, weak bands could still be observed. When the temperature was raised to 973 and 1023 K, no bands were observed even though the sample was under O_2 (spectra (g) and (h)).

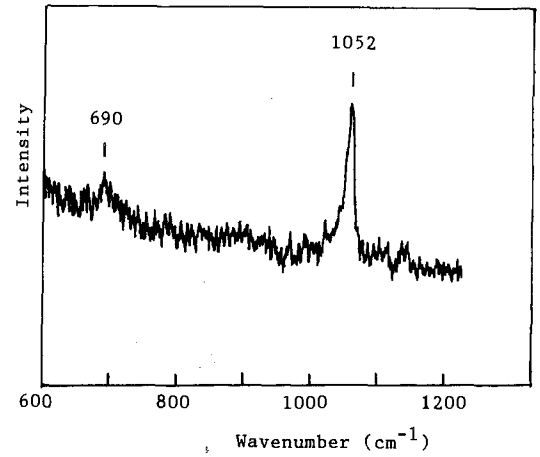

Fig. 2. Raman spectrum of a SmOF sample heated in H_2 for 2 h at 1023 K and being exposed to CO_2 (1 atm) at 298 K.

When CO_2 was admitted to SmOF at 303 K, two Raman bands due to CO_3^{2-} in-plane bending and symmetric stretching vibrations could be observed respectively at 690 and 1052 cm^{-1} (fig. 2). These two bands disappeared around 750 K. Similar bands were observed by Lunsford et al. [2] at 689 and 1051 cm^{-1} over BaO/MgO. We performed a CO_2-TPD experiment and found that CO_2 desorption from SmOF diminished at ca. 850 K (fig. 3). Since the SmOF sample was pretreated by purified hydrogen, helium and oxygen at 973 K before Raman characterization, we are pretty sure that the results in fig. 1 are free from CO_2 contamination.

Before discussing any further, it may be helpful to recall that Eysel and Thym [4] suggested that the vibrational frequency for surface peroxide (O_2^{2-}) lied in the region of 730–950 cm^{-1} while Valentine [5] suggested that perturbed intermediate oxygen species O_2^{n-} ($1 < n < 2$) should give rise to bands in the 900–1100 cm^{-1} region. In order to be more precise, we performed Raman examinations on BaO_2 and CsO_2 and observed bands at 840 and 1122 cm^{-1} respectively (fig. 4). Hence O_2^{2-} and O_2^- species should have Raman bands at ca. 840 and 1122 cm^{-1}. Bands recorded between these two wavenumbers should be the O_2^{n-} species, intermediate between O_2^{2-} and O_2^-. Furthermore, since the vibrational frequency for neutral O_2 was known to be

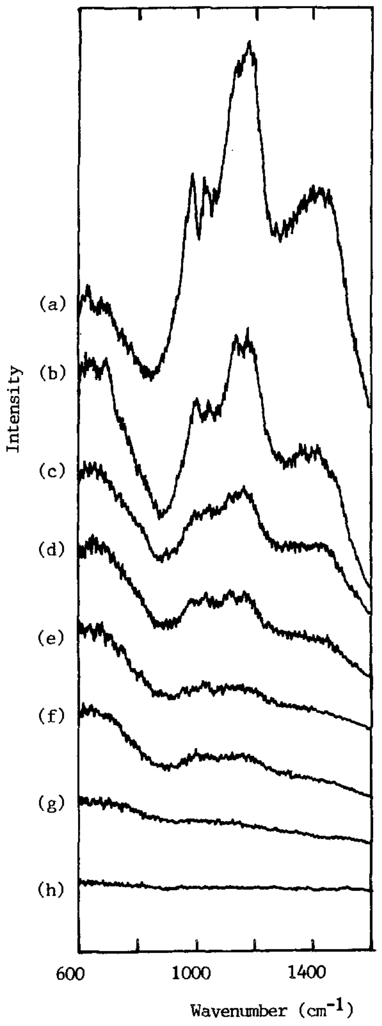

Fig. 1. Raman spectra of a SmOF sample heated in H_2 (973 K, 1 h) and helium (973 K, 1 h) and cooled in oxygen to (a) 303 K, and heated in oxygen stepwise to (b) 473 K, (c) 573 K, (d) 673 K, (e) 773 K, (f) spectrum obtained at 773 K in helium, (g) 973 K, and (h) 1023 K.

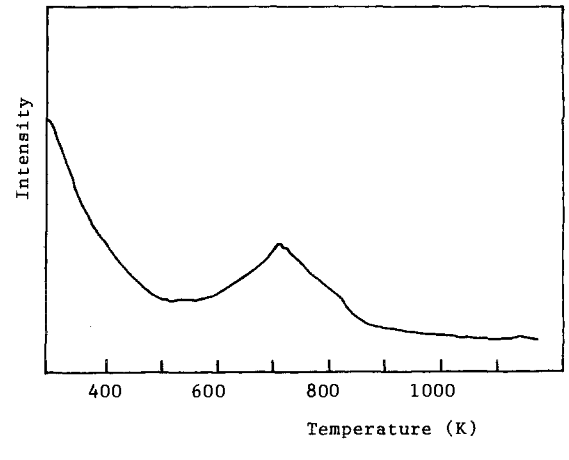

Fig. 3. TPD spectrum of CO_2. The SmOF sample was exposed to CO_2 at 303 K for 25 min. It was then purged by He for 20 min before heating to 1173 K for desorption.

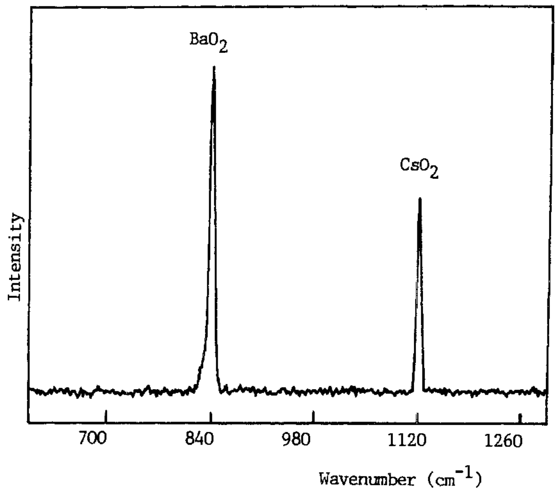

Fig. 4. Laser Raman spectrum of of a mixture of BaO_2 and CsO_2.

around 1550 cm^{-1} [6], Raman bands observed within the 1200–1452 cm^{-1} range might be ascribed to $O_2^{\delta-}$ ($0 < \delta < 1$), species intermediate between O_2^- and neutral O_2. Accordingly, we assign the bands at 984 and 1026 cm^{-1} in fig. 1 respectively to O_2^{2-} and O_2^{n-}. The band at 1128 is ascribed to O_2^- species. Since Bösch and Kanzig reported that NaO_2 showed a band at 1164 cm^{-1} [7], we assign the 1184 cm^{-1} band to O_2^- as well. As for the bands at 1402 and 1460 cm^{-1}, they are assigned to $O_2^{\delta-}$ species.

Besides the bands in the 880–1550 cm^{-1} range, we observed band(s) at ca. 668 cm^{-1}. Such wavenumber is lower than the usual vibration of surface O_2^{2-}. Tentatively, we assign them to sublayer O_2^{2-} species existing in the lattice of SmOF. Our assignment is not without reason. Islam and Ilett [8] had performed computer simulations on the {001} and {011} surfaces of La_2O_3. They suggested that it is possible for subsurface O^- species to couple. According to their calculation, chemical binding exists between two neighbouring O^- ions and the O–O bond strength is determined by the O–O distance. In a paper about $BaPbO_3$, Kharas and Lunsford [9] suggested that nonclassical dioxygen species with O–O contacts of ca. 3 Å could have existed inside the $BaPbO_3$ lattice. We estimate that the separation of two neighbouring sublayer O^- ions inside the SmOF lattice should be larger than the O–O distance (ca. 1.47 Å) of surface peroxide and consequently the wavenumber of the former is lower than the latter. The increase in intensity of the 668 cm^{-1} band and the simultaneous decrease of the band intensity in the 880–1550 cm^{-1} range between 303 and 473 K could be a result of diffusion of surface dioxygen species towards the sublayer level (fig. 1, spectra (a) and (b)).

Fig. 5 shows the TPD spectrum of O_2. Before the TPD experiment was performed, the SmOF sample (0.2000 g) was first heated in oxygen (ca. 1 atm) at 1073 K for 1 h, then cooled in oxygen to 303 K and purged by helium at the same temperature for 15 min. There was no desorption below 973 K. Above 973 K, oxygen desorbed and the desorption peak was at 1095 K.

Based on the TPD result, the disappearance of Raman signals at 973 K is not due to oxygen desorption. However, it is apparent that as the sample temperature was raised, the Raman signal reduced in intensity and at 973 K no signal remained even though the sample was under an atmosphere of oxygen (fig. 1). The dioxygen species which were originally observable must have changed to something undetectable by Raman spectrometry. The most reasonable explanation is that due to thermal excitation, dioxygen species were converted to mono-oxygen species. Above 973 K, the energized mono-oxygen species coupled and desorbed as O_2. We

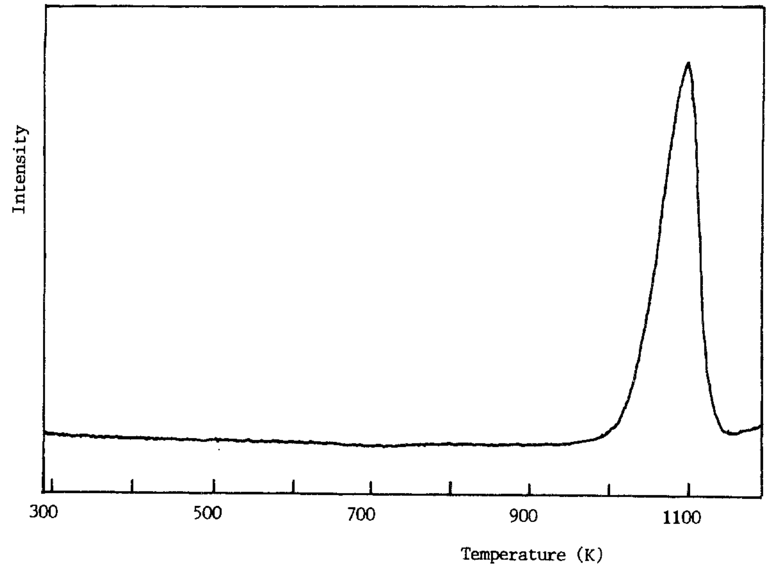

Fig. 5. TPD spectrum of O_2. Please refer to the text for sample treatment before desorption.

tried to identify the mono-oxygen species by EPR but failed. Under treatments similar to the Raman experiments, no EPR signals of oxygen species could be obtained over the SmOF sample. What we could see were wide peaks with width around 3000 Gauss. Perhaps the spin–spin interaction between paramagnetic Sm^{3+} and oxygen species such as O^- and O_2^- has widened the EPR signals of the oxygen species, rendering them undetectable.

3.2. Ethane dehydrogenation

Table 1 shows the results of ethane oxidative dehydrogenation at 773 and 873 K when 60 μl of $C_2H_6/^{18}O_2$ (2/1 molar ratio) mixture was pulsed into the reactor with 0.2000 g of catalyst. One can see improvement in both ethane conversion (from 6.5 to 15.3%) and C_2H_4 selectivity (from 12.3 to 31.1%) as the reaction temperature was raised from 773 to 873 K. The ethene yield at 873 K was 4.8%. Without the catalyst, a blank reactor showed no reactivity whatsoever at 873 K. At 925 K, however, a blank reactor would give an ethane conversion of 9.2% and C_2H_4 selectivity of 11.8%, resulting in a C_2H_4 yield of 1.1%. Hence, above 873 K, gas phase reaction became significant. That is why we kept the reaction temperature at or below 873 K. The original idea of using $^{18}O_2$ was to differentiate the participation of gaseous oxygen ($^{18}O_2$) versus ^{16}O of SmOF. It turned out to be a futile exercise. At 873 and 973 K, although the ^{18}O-containing products constituted to less than 2% of the total amount of H_2O, CO_2, and CO produced, we cannot conclude that the gas phase reaction was insignificant. The reason is that when we pulsed $C^{18}O$ and $C^{18}O_2$ into the reactor with the catalyst at these temperatures, a significant amount of $C^{16}O$ and $C^{16}O_2$ was generated. In other words, $C^{18}O$ and $C^{18}O_2$ exchanged with ^{16}O of SmOF to produce $C^{16}O$ and $C^{16}O_2$. Since CO and CO_2 are co-products of C_2H_6 oxidation, the origin of reacting oxygen cannot be inferred.

If 50 μl of pure ethane was pulsed in at 773 K to a sample pretreated with O_2 at 973 K for 10 min and purged with helium for 10 min, ethane conversion was 0.3% and CO_2 was the sole product. At 873 K, ethane conversion was 1.4% while the C_2H_4 selectivity was 83.2%. At 973 K, ethane conversion was 8.2% and C_2H_4 selectivity was 91.8% (table 2). The very fact that CO, CO_2 and H_2O were generated confirms that oxygen was present on SmOF and indeed served to catalyze the reaction even though both Raman and EPR could not detect any oxygen species at 973 K. Under similar conditions in the absence of the SmOF sample, a blank reactor showed no reactivity whatsoever. Based on the Raman results, the amount of surface dioxygen species was minimal at 973 K. We conclude that the mono-oxygen is responsible for the high C_2H_4 selectivity obtained at 973 K.

Table 1
The results of $C_2H_6/^{18}O_2$ (2/1) interaction over SmOF

Temp. (K)	Conversion of C_2H_6 (%)	Selectivity (%)				C_2H_4 yield (%)
		CO	CO_2	CH_4	C_2H_4	
773	6.5	49.0	38.7	0	12.3	0.8
873	15.3	21.2	47.7	0	31.1	4.8

Table 2
The interaction of pure C_2H_6 with a SmOF sample treated with oxygen and helium at 973 K

Temp. (K)	Conversion of C_2H_6 (%)	Selectivity (%)				C_2H_4 yield (%)
		CO	CO_2	CH_4	C_2H_4	
773	0.3	0	100.0	0	0	0
873	1.4	8.6	8.1	0	83.2	1.2
923	4.1	8.5	0.7	0.7	90.0	3.69
973	8.2	3.5	4.4	0.3	91.8	7.5

4. Conclusion

At 303 K, O_2 adsorbs largely as O_2^{2-}, O_2^{n-} ($1 < n < 2$), O_2^-, and $O_2^{\delta-}$ ($0 < \delta < 1$) on the surface of SmOF. As the sample temperature was raised to 973 K, dioxygen species are converted to mono-oxygen species which are undetectable by laser Raman spectrometry. The mono-oxygen species is concluded to be responsible for the generation of C_2H_4 in ethane oxidative dehydrogenation reaction over the SmOF catalyst.

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