FT Raman Study of the Surface Oxygen Species on the BaX_2 (X=F, Cl) Promoted Y_2O_3 and Nd_2O_3 Catalysts for the Oxidative Dehydrogenation of Ethane

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The BaX_2(X=F, Cl) promoted Y_2O_3 and Nd_2O_3 catalysts for the oxidative dehydrogenation of ethane(ODE) have been studied by using FT-Raman spectroscopy in light of formation, types, stability and reactivity of the surface oxygen species involved in various atmosphere at different temperatures or the ODE reaction.

The oxidative dehydrogenation of ethane (ODE) has been reported using the alkali metal and alkaline earth metal oxides,[1,2] the transition metal oxides,[3,4] the rare-earth metal oxides,[5,6] and other catalytic materials.[7] The use of gaseous oxygen provides the thermodynamic driving force which permits the reaction to be conducted at lower temperature than a simple dehydrogenation without oxygen. Previous research revealed that the rare earth metal oxides promoted with alkaline earth metal halogens exhibit good performance in the ODE reaction.[8] In this letter, the FT-Raman results are reported herein for the BaX_2(X=F, Cl) promoted Y_2O_3 and Nd_2O_3 catalysts used for the ODE reaction. The study is in light of formation, types, stability and reactivity of the surface oxygen species involved in various treatments or the ODE reaction.

30 mol% $BaCl_2/Y_2O_3$ and $BaCl_2/Nd_2O_3$ catalysts were prepared by impregnating the commercial Y_2O_3 and Nd_2O_3 with a solution of $BaCl_2{\cdot}2H_2O$. 30 mol% BaF_2/Y_2O_3 catalyst was prepared by grinding the BaF_2 and Y_2O_3 powder with small amount of water till a paste was obtained. The materials then were dried at 383 K for 6 h and calcined in air at 1073 K for 5 h. For the catalysts studied, no appreciable change from chloride to oxide was found by either Raman or IR spectroscopes after calcination or oxidation. FT Raman was conducted on Nicolet 910 FT Raman spectrometer with 65 scans at 4 cm^{-1} resolution. Two especially designed micro-reactors were used for Raman measurement. One can be operated "in situ" during the reaction. Unfortunately, however, the Raman signal from the sample cannot be successfully recorded because of very serious thermal background at elevated temperatures. Thus we have to use another type of reactor in which the catalyst can be treated in different atmosphere from room temperature to 1073 K or can be operated under the steady-state reaction. After that the catalyst was transferred into the test tube for Raman measurement at room temperature without expose to air. Although the study was not "in situ" in this way, the results obtained are still interesting and informative.

For the $BaCl_2$ promoted Y_2O_3, the results are shown in Figure 1. The calcined sample showed several small bands in the 1084-1178 cm^{-1} range. As the catalyst was first heated in nitrogen to 873 K and kept there for 20 min then switched to oxygen, a broad band in the 900-1200 cm^{-1} range appeared, and the small bands in the 1084-1178 cm^{-1} became more intensive. This broad band is likely due to the coexistence of several types of surface oxygen species, mainly the O_2^{n-} form(1<n<2) as well as O_2^-.[9,10] The small bands are likely due to O_2^- species on the Y_2O_3 component when compared with the pure Y_2O_3 sample(not shown). The broad band becomes more intensive as the sample was further heated in oxygen to 1023 K, and appears weak when the sample was exposed into the reaction mixture at 873 K. When the sample was treated again in oxygen at 1023 K after reaction, the broad band appears most intensive accompanied by another small band at ~740 cm^{-1} which might be ascribed to the O_2^{2-} species.[11,12] The surface dioxygen species might be related to the surface barium ions and could be stabilized at high temperatures. However, these Ba-containing assembles are not exactly the BaO_2 phase.[12,13] If this sample was exposed to pure ethane at 873 K, both the broad band and the small band at ~740 cm^{-1} disappeared almost completely, while the bands in the 1084-1178 cm^{-1} range were still presented though their intensity slightly decreased. This observation revealed that the surface O_2^{2-}, O_2^{n-}(1<n<2) and O_2^- species are all able to convert the ethane reactant. Because of the promotion effect of the $BaCl_2$ component, new kinds of oxygen species were developed and their reactivity was improved. On the other hand, the reactivity of O_2^- species on the unpromoted Y_2O_3 sample is relatively low. The steady state catalytic data (not present here) further confirmed this conclusion. Moreover, an equilibrium between the oxygen adspecies and the gaseous oxygen molecules might be set up quickly as the gaseous oxygen was supplied, which allows a certain amount of oxygen adspecies present on the catalyst

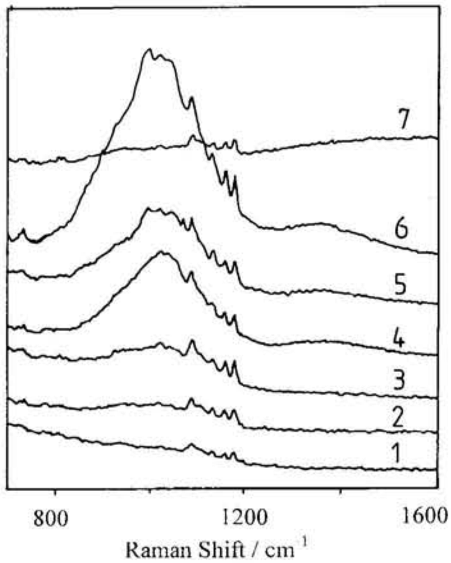

Figure 1. FT-Raman spectra of the 30 mol%$BaCl_2/Y_2O_3$. (1) calcined sample, at 298 K, (2)treated in N_2 at 873 K, (3)in O_2 at 873 K, (4)in O_2 at 1023 K, (5)in the reaction mixture at 873 K, (6)in O_2 at 1023 K again, (7)in pure ethane at 873 K.

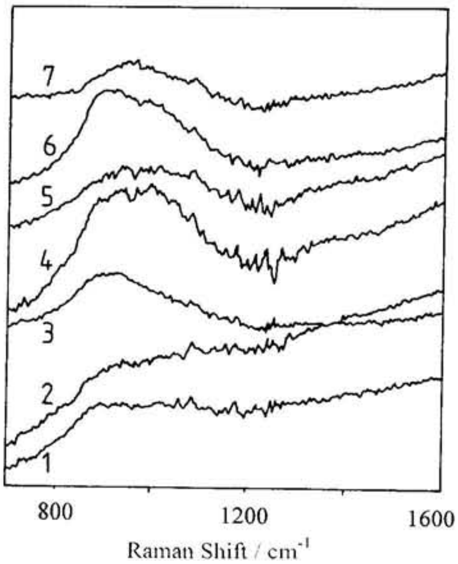

Figure 2. FT-Raman spectra of the 30 mol%BaF_2/Y_2O_3. (1) calcined sample, at 298 K, (2)treated in N_2 at 873 K, (3)in O_2 at 873 K, (4)in O_2 at 1023 K, (5)in the reaction mixture at 873 K, (6)in O_2 at 1023 K again, (7)in pure ethane at 873 K.

surface.

For the BaF_2 promoted sample, the situation is principally similar to the $BaCl_2$ promoted sample, seen in Figure 2. The surface concentration of oxygen adspecies has been increased due to the addition of the BaF_2 component. However, what differing from the observation made on the $BaCl_2/Y_2O_3$ system is that the proportion of the O_2^{n-} species should be considerably increased among the dioxygen adspecies and some O_2^{2-} species might be included in the broad band, since the band position was significantly shifted toward the low wave end.

For the calcined sample of $BaCl_2/Nd_2O_3$ without any treatment, two Raman bands at 867 and 920 cm^{-1} can be observed, they are probably due to the O_2^{2-} and $O_2^{n-}(1<n<2)$ species respectively.[9] The different wave numbers of dioxygen species on the $BaCl_2/Nd_2O_3$ indicates that different kind of support also affects and modifies on the nature of surface oxygen species. Compared with the unpromoted Nd_2O_3, it can be concluded that these two bands do not originate from the Nd_2O_3 component. If the catalyst was heated in oxygen at very high temperature, namely, 1023 K, these two bands became very intensive and slightly shifted toward the high wave end. In addition, another small and broad band centered at 1275 cm^{-1} appeared, which was likely due to the $O_2^{\delta-}(0<\delta<1)$ species.[14] When the sample was treated in nitrogen at 873 K, the Raman bands significantly decreased the intensity, indicating the considerable desorption of surface oxygen species. When the N_2-treated sample was heated again in oxygen at 873 K, the oxygen adspecies only partly recover. The surface oxygen species can be completely eliminated by hydrogen treatment at 1023 K, and cannot be fully recovered in the oxygen atmosphere at elevated temperatures after H_2-treatment, possibly due to the alteration in surface state of catalyst. Seen in Figure 3, if the catalyst was first treated in oxygen then heated in the reaction mixture at elevated temperatures, the amount of surface oxygen species was increased with increasing temperature and reached the maximum at around 833 K. Meanwhile a notable shoulder appeared at 1039 cm^{-1}, revealing the formation of O_2^- species. In the reaction atmosphere, the increase in the amount of surface oxygen species is probably due to the presence of reductive hydrocarbon molecule(C_2H_6) as well as the elevated temperature for activation. When the reaction temperature was further increased up to 873 K, the intensity of the bands was considerably reduced and the 1039 cm^{-1} shoulder was almost disappeared, indicating that the reaction procedure was facilitated at higher temperature at the expense of surface oxygen species. If the Raman features of the dioxygen species are correlated with the catalytic performances(not included here), it made us to tentatively conclude that on the certain catalysts we studied, the $O_2^{\delta-}$ $(0<\delta<1)$, the O_2^- and the higher wave number O_2^{n-}(1<n<2, its property is more analogous to that of O_2^-) are mainly responsible for the higher ethane conversion, while the O_2^{2-} as well as the lower wave number O_2^{n-}(1<n<2, its property is more similar to that of O_2^{2-}) seems to be principally for the higher ethene selectivity.

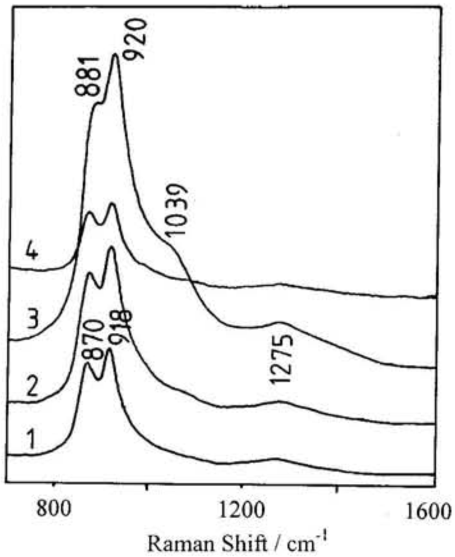

Figure 3. FT-Raman spectra of the 30 mol% $BaCl_2/Nd_2O_3$ after the ODE reaction at elevated temperatures. (1)after treated in O_2 at 873 K, (2)in the reaction mixture at 773 K, (3)at 833 K, (4)at 873 K.

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