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X-Ray Photoelectron Spectroscopic Studies of Lanthanum Oxide Based Oxidative Coupling of Methane Catalysts

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X-Ray photoelectron spectroscopic studies of lanthanum oxide based oxidative coupling of methane catalysts, indicate a high binding energy O(1s) peak at 532.6-533.2 eV, which is strong evidence for surface superoxide (O_2^-) or peroxycarbonate ($CO_4^=$).

We have previously reported that oxidative coupling of methane (OCM) cofeed catalysts are insulating solids at room temperature and p-type semiconductors (conduction by holes) at high temperature.$^{1)}$ The majority of these catalysts (such as those based on alkali, alkaline earth, lanthanum and samarium oxides) are also irreducible, highly carbonated solids with elevated O_2 and CO_2 adsorption coefficients. Oxygen adsorption must involve redox reactions between oxygen species, and probably occurs through the following elementary surface processes.

$$V_O^{\bullet\bullet} \rightleftharpoons V_O^{\bullet} + h^+ \quad (1)$$

$$V_O^{\bullet} + O_2(gas) \rightleftharpoons O_2^- \quad (2)$$

$$V_O^{\bullet} + O_2^- \rightleftharpoons O_2^= \quad (3)$$

$$O_2^= \rightleftharpoons 2O^- \quad (4)$$

$$O^- \rightleftharpoons O^= + h^+ \quad (5)$$

In the equations above, $V_O^{\bullet\bullet}$ represents an oxygen vacancy which is not associated with an electron, $V_O^{\bullet}$ an oxygen vacancy associated with one electron (also referred to as an F center), and h^+ a positive charge carrier. The latter may be regarded, for example, as surface or bulk O^-. The reactions shown in Eqs. 2 and 3 consume surface oxygen vacancies. Thus, for oxides in which the cation is unable to change oxidation state, as surface coverage increases (i.e. as surface oxygen vacancies become limited), oxygen adsorption will directly depend on the equilibrium of Eq. 2. Both superoxide $(O_2^-)^{2)}$ and peroxide $(O_2^=)^{3)}$ have been proposed as potential initiators for the abstraction of an hydrogen atom from CH_4 to generate CH_3 radicals on rare earth oxides.

We have examined several OCM catalysts using XPS in an attempt to corroborate EPR evidence for the existence of superoxide associated with La_2O_3.$^{2)}$ Samples of La_2O_3 and 1 and 3% Sr/La_2O_3 were prepared by dissolving lanthanum carbonate, alone or with strontium nitrate, in concentrated acetic acid. The mixtures were evaporated to dryness at 140 °C, then calcined in air at 570 °C for 1 h. A sample of 15% Ba/La$_2$O$_3$ was prepared by evaporating to dryness a mixture of La$_2$O$_3$ and barium ethoxide in absolute ethanol, then heating at 200 °C under vacuum. The samples were pretreated under a flow of 20% O$_2$/Ar for 1 h at 900 °C before being transferred via glove bag to the XPS pre-treatment chamber. Samples were subjected to XPS analyses before and after *in situ* treatments with H$_2$/Ar (1 h) 650 °C and with O$_2$/Ar (1 h) 650 °C. In all twelve XPS analyses, the surfaces were found to be substantially carbonated (between 15 and 45% of the surface O(1s) was $CO_3^{=}$).

The binding energy (BE) of adventitious carbon (284.6 eV) was used as the reference for all experiments. Carbonate C(1s) was positioned at 288.9 eV and normal lattice oxygen ($O^{=}$) at 528.8-529.0 eV. In order to fit the O(1s) region, the ratio of carbonate O(1s) to carbonate C(1s) was defined to be 3. The curve fit of the O(1s) region could not be accomplished with less than four different oxygen species, using an 80% Gaussian - 20% Lorentzian peak shape. The positions of these peaks are: 528.8-529.0 ($O^{=}$); 530.9-531.2; 531.6-531.7 ($CO_3^{=}$); and 532.6-532.8 (pure or Sr doped samples) or 533.0-533.2 (15% Ba doped sample). The peak located at 530.9-531.2 eV cannot be unambiguously identified, but is certainly due to either O^-, OH^-, or $O_2^{=}$. The peak at high BE decreases in intensity (as much as 25%) after H$_2$ treatment, but increases after subsequent reoxidation. This peak also increases in intensity upon the addition of an alkaline earth cation, and as a result increasing concentration of surface carbonate, Fig. 1. This is in agreement with the hypothesis that the addition of an M^{n+} metal into an $M^{(n+1)+}$ matrix, of similar radius, should increase the number of defect sites.

In view of both the high BE of this species and its subsistence after high temperature treatments in H$_2$ and subsequently in O$_2$, it is unequivocally attributed to a chemisorbed dioxygen species rather than a monoatomic oxygen or physisorbed species. (Note that the ratio of the two highest energy O(1s) peaks to the carbonate C(1s) peak is in excess of 3 for all spectra. Thus, the highest energy O(1s) peak cannot be explained by nonuniform sample charging). Although the absolute identification of the dioxygen species cannot be determined, it is likely to be due to either O_2^- or $CO_4^{=}$ (peroxycarbonate, $[O_2COO]^{=}$). The latter species has been synthesized in bulk form by reacting Na, K, or Ba peroxides in CO$_2$ 4a,b) or heating BaO at 900 °C in air for over 35 h.4c) The partial charge on the terminal peroxo-oxygen should be substantially less negative than the three carbon bound oxygens and therefore shifted to higher BE.

The difference in BE between lattice oxygen and other oxygen species (δ) is often a better indication of the type of oxygen species rather than its absolute value, as the latter depends on the linearity of the individual instrument and the metal oxide. XPS studies on species which are considered to possess $O_2^{=}$, invariably have δ values which are close to 3 eV: BaO$_2$(533.0, δ=3.2),5) PbO$_2$(532.7, δ=3),6) BaBiO$_3$(532.4, δ=3.1),6) SrPbO$_3$(532.5,δ=2.9),6) BaPbO$_3$ (532.5, δ=2.7)5) and (532.4, δ=3.1).6)

Recent XPS and UPS studies of oxygen species on metal surfaces have identified a diatomic oxygen species at 532.8-533.2 eV (δ =4-4.5 eV): Cs/Ag (533.0, δ =4.5),[7] K/Ag(533.0, δ =4.0,[8] Ba/Ag(533, δ =4.4),[8] K(532.8, δ = 4.2),[9] Cs/Ni(533.0, δ =4).[10] This species has been attributed to O_2^- by UPS.[10,11] In view of the similarity between these values and those of the present study (δ =3.6-4.1 pure or Sr doped, 4.1-4.3 Ba doped La_2O_3), it is possible that appreciable quantities of surface O_2^- ions exist on La_2O_3 based OCM catalysts; however, there is sufficient circumstantial evidence to suggest that the high BE peak may actually be due to surface $CO_4^=$.

The following points are noteworthy: 1) selective OCM cofeed catalysts are often irreducible, highly carbonated metal oxides, 2) O^-, O_2^-, and O_3^- have been detected by EPR spectroscopy on the surface of Li/MgO[12] and O_2^- on La_2O_3,[2] 3) a high BE O(1s) peak, attributed to a surface dioxygen ion, either O_2^- or $CO_4^=$, has been found on pure and alkaline earth doped La_2O_3 surfaces, and 4) this O(1s) peak increases in intensity with increasing surface carbonate coverage. These common points lead us to suggest that an equilibrium between surface carbonate and surface superoxide ions may exist, Eq. 6.

$$CO_3^= + O_2^- \rightleftharpoons CO_4^= + O^- \qquad (6)$$

The presence of surface carbonate reduces the number of available $V_O^\bullet$ sites. The low relative probability of finding two adjacent $V_O^\bullet$ centers (required for the formation of $O_2^=$) at high carbonate and oxygen coverage would favor initial surface O_2^- formation. Considering the coexistence of both surface $CO_3^=$ and O_2^- and the lack of a charge transfer mechanism with the cations, a surface mechanism such as Eq. 6 is attractive for several reasons: 1) O_2^- ions contained in peroxides have been shown to be relatively ineffective for methane activation;[13] 2) this

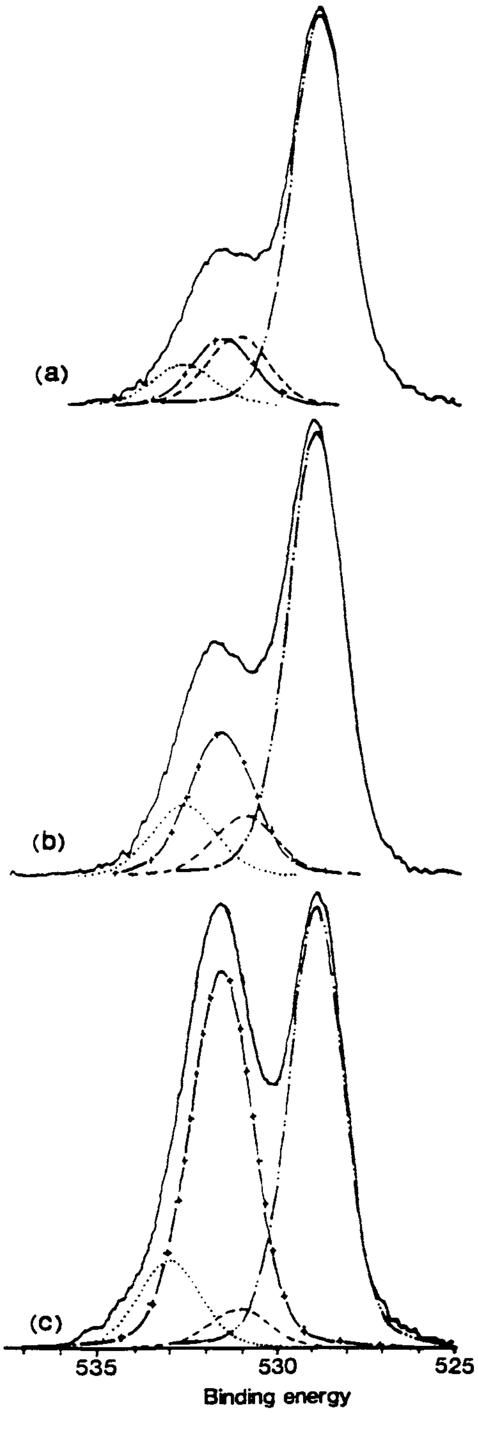

Fig. 1. XPS O(1s) spectra of (a) pure, (b) 3% Sr doped, and (c) 15% Ba doped La_2O_3 after *in situ* treatments with H_2/Ar then O_2/Ar. The O(1s) peaks, by order of increasing BE, are attributed to: $O^=$, undefined, $CO_3^=$ and a dioxygen species. The full with at half maxima are 2.0±0.1 eV.

equilibrium would explain the loss of the O_2^- EPR signal on La_2O_3 when the sample is not rigorously decarbonated,14) as $CO_4^=$ would be EPR inactive; and 3) carbonate assisted destruction of O_2^- would shift the surface oxygen equilibrium to Eq. 4.

The previously proposed equilibrium (Eq.7) between O_2 and CO_2 in molten carbonate salts,15) which are known to be OCM catalysts,16) may also involve the intermediate formation of $CO_4^=$.

$$O_2 + 2CO_3^= \rightleftharpoons 2CO_2 + O_2^= \qquad (7)$$

Although it is unlikely that $CO_4^=$ is an active species for methane activation, it may promote the formation of previously proposed active species such as O^- *via* Eq. 6, $O_2^=$ *via* Eqs. 6 and 4, or $O_2^=$ by a more complex equilibrium such as that shown in Eq. 7 . O^-, however, has not been detected by EPR spectroscopy on La_2O_3 OCM catalysts.

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