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LOW TEMPERATURE CATALYSTS MODIFIED BY F^- FOR THE OXIDATIVE COUPLING OF METHANE

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FB, FC and FD, FE catalysts were prepared from 2g LaF_3 with 0.88g, 0.43g CeO_2 and 1.3g, 0.66g ThO_2 respetively. Coupling reactions were carried out in a fixed bed quartz reactor. The reaction conditions were as follows: 0.2ml catalyst loading; methane/oxygen ratio=3, no inert gas; feed flow rate=50ml/min. The catalysts were characterized by XRD, XPS, ESR, Raman and TPD.

CeO_2 is a total oxidation catalyst for the oxidative coupling of methane (OCM). ThO_2 and LaF_3 are inactive for OCM under 650℃. After being modified by the addition of LaF_3, they could convert CH_4 to C_2 hydrocarbons selectively at 480-550℃. C_2 yields of 14.7%, 13.4% with C_2 selectivity of 52.1%, 55.4% were achieved on FB, FC catalysts at 500℃, respectively. FD and FE catalysts gave C_2 yields of 11.6% and 14.0% with C_2 selectivity of 40.8% and 45.1% at 500℃, respectively.

XRD measurements show that FB, FC catalysts consisted of LaF_3, CeO_2 and tetragonal LaOF phase; FD, FE catalysts consisted of ThO_2, tetragonal LaOF and LaF_3. These results indicate O^{2-} in CeO_2 and ThO_2 exchanged with F^- in LaF_3 in some way. The new tetragonal LaOF phase is a superstructure of fluorite, which may be favorable to activating CH_4 at low temperature.

Results from XPS show that only O^{2-} peaks were observed on the surface of CeO_2 and ThO_2, however, three peaks were observed on the surface of FB and FD, which may be assigned to O^{2-}, O^- (or O_2^{2-}) and O_2^- species. Raman spectra indicate that no peak was observed on the surface of no oxygen adsorbed ThO_2, LaF_3, FB and FC. After being adsorbed with oxygen, some peaks attributed to O_2^- or O_2^{n-} ($1<n<2$) were observed on the surface of FB and FC. Peaks attributed to O_2^{2-}, O_2^-, O_2^{n-} ($1<n<2$), $O_2^{\delta-}$ ($0<\delta<1$) were observed on the surface of FD, FE either with or without adsorbed oxygen, but the peaks with oxygen adsorbed were stronger than those without adsorbed oxygen. There was no peak of ESR on FB and FC without adsorbed oxygen. Correspondingly, the peaks attributed to O^- or O_2^- were observed on FB and FC adsorbed with oxygen. No peak of ESR was observed on FD and FE, which may be resulted from the coupling of higher surface concentration oxygen species. TPD spectra of FB gave O_2^- peak, but FC gave a weak O_2^{2-} peak besides the O_2^- peak. Three peaks attributed to O_2^-, O_2^{2-} and O_2^{n-} (or O^{2-}) were observed on the TPD spetra of FD.

On the whole, the results obtained from the various spectra are the same. O_2^- and few O_2^{2-} are main active oxygen species on the surface of FB and FC. Besides O_2^-, O_2^{2-} and O^-, the oxygen species such as O_2^{n-} ($1<n<2$) and $O_2^{\delta-}$ ($0<\delta<1$) may be also the active oxygen species over FD and FE. The existence of these active oxygen species might be favorable to the activation of CH_4 at low temperature.