XRD and In-situ Synchrotron Radiation XRD Studies on the phase transition of the Oxidative Coupling of Methane Catalysts

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Abstract

XRD and in-situ synchrotron Radiation X-ray diffraction technology are employed to study the phase transition of the oxidative coupling of methane (OCM) catalysts including SrF_2/La_2O_3 and Na-W-Mn/SiO_2. The 20% SrF_2/La_2O_3 catalyst before and after the reaction was characterized by XRD and Raman spectroscopy. The reason for the improvement of the performance of La_2O_3 catalyst after doping SrF_2 was studied. The phase transitions of the Na-W-Mn/SiO_2 OCM catalysts are investigated by in-situ XRD under the reaction conditions.

The crystal structures of the samples were recorded by XRD analysis on Bruker AXS D8 Advance SSS X-ray diffractometer, using CuKα radiation (40KV and 300mA). Anton Parr XRK900 reaction chamber was equipped, which was used to heat samples from room temperature to 900℃ and provide certain experimental conditions.

Temperature-programmed experiments in conjunction with XRD were performed at beamline X7B (λ=0.3196A) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The reaction of samples under 5% O_2 in He and 20% CH_4 in He was studies in a quartz capillary mounted in a flow cell system. Quartz wool was added to both ends of the sample to keep its position under gas flow. In the experimental setup for TP, a resistance heating coil enclosed the sample capillary, and a Type K thermocouple was placed inside the capillary in the quartz wool next to the sampled. A temperature controller reads the temperature of the thermocouple and adjusted the output voltage applied to the heating coil. Samples were heated from room temperature to 850℃ at a rate 10℃/min. A Perkin Elmer Amorphous Silicon Detector was used to collect two-dimensional transmission diffraction data, which were subsequently processed with the program Fit2D to obtain XRD profiled.

After doping SrF_2 into La_2O_3 catalyst, the activity of the catalyst is obviously improved. 20% SrF_2/La_2O_3 catalyst is more favorable to oxygen adsorption and activation due to the exchange of F ions with lattice O during the reaction process, so the conversion and selectivity of the catalyst doped with 20% SrF_2 are higher than those without doping.

In-situ Synchrotron Radiation XRD methods were used to follow the structural changes that occur during the OCM reaction of CH_4 and O_2 over Na-W-Mn/SiO_2。Experimental results show there exist different crystal structures of the catalysts under different temperature. The elements of W and Mn are the key factors to affect the crystal structure changing of the catalysts, moreover the crystal structures under 850℃ be of OCM catalytic activity.