MASTER'S THESIS

Methane oxidative coupling over fluoride/oxide catalysts: a dissertation

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METHANE OXIDATIVE COUPLING OVER FLUORIDE/OXIDE CATALYSTS

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ABSTRACT

The oxidative coupling of methane (OCM) was studied by heterogeneous catalysis over several fluoride/oxide catalysts. The catalysts tested include NaF/MgO, NaF/ZrO_2, NaF/La_2O_3 and LaF_3/La_2O_3 (first named component dispersed on the second). The specific surface area of catalysts was measured by BET method. XRD and XPS were employed to characterize the nature of the catalysts.

For the catalysts loaded with NaF, poor NaF dispersion and poor catalytic activity were observed in the cases of NaF/MgO and NaF/ZrO_2; while complete NaF dispersion and enhanced activity were observed in the case of NaF/La_2O_3. The activities of the catalysts were related to the variation of specific surface area. The effects of reaction conditions were studied and the maximum C_2 yield of 18.4% was obtained over 20mol%NaF/La_2O_3 at 1023K, with CH_4:O_2=2.6:1 and W/F=1.8 g·sec/ml.

For the LaF_3/La_2O_3 catalysts, it was detected that the catalysts were mainly rhombohedral LaOF (when LaF_3 content was less than or equal to 50mol%) or tetragonal LaOF (when LaF_3 content was larger than 50mol%). The 50mol%LaF_3/La_2O_3 was found active even at 873K. At 1023K, the C_2 yield was 12.7% at 49.1% C_2 selectivity. It was found to be stable and had a life-time not less than 50 h at 1023K. The activation energies for CH_4 conversion and C_2 formation at high O_2 conversion were 2.6 and 11.3 kcal/mol respectively. It is suggested that the catalyst has ample stoichiometric defects and generates active oxygen sites suitable for OCM.

In addition, OCM was also studied by electrocatalysis with yttria-stabilized zirconia (YSZ) solid electrolyte cell over 50mol%LaF_3/La_2O_3 and Au mixed 50mol%LaF_3/La_2O_3 catalysts at 923-1023K. The maximum C_2 yield obtained was 5.4% at 1023K over the 50mol%LaF_3/La_2O_3. The effect of electrochemical oxygen pumping (EOP) on C_2 selectivity and rates of formation of products were studied over both catalysts. Obvious enhancement was observed at 973K over (50mol%LaF_3/La_2O_3)/Au (1/1) mixed catalyst. It was considered that the methane coupling process involved both gas-phase and surface reaction. EOP can only modify the surface reaction by the generation of active oxygen species.

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