

MASTER'S THESIS

Methane oxidative coupling over fluoride/oxide catalysts: a dissertation

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**METHANE OXIDATIVE COUPLING
OVER FLUORIDE/OXIDE CATALYSTS**

A Dissertation submitted

by

Zhang Yi Qun

In partial fulfillment of the requirements

for the degree of

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in

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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/ZrO₂, NaF/La₂O₃ and LaF₃/La₂O₃ (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/ZrO₂; while complete NaF dispersion and enhanced activity were observed in the case of NaF/La₂O₃. The activities of the catalysts were related to the variation of specific surface area. The effects of reaction conditions were studied and the maximum C₂ yield of 18.4% was obtained over 20mol%NaF/La₂O₃ at 1023K, with CH₄:O₂=2.6:1 and W/F=1.8 g·sec/ml.

For the LaF₃/La₂O₃ catalysts, it was detected that the catalysts were mainly rhombohedral LaOF (when LaF₃ content was less than or equal to 50mol%) or tetragonal LaOF (when LaF₃ content was larger than 50mol%). The 50mol%LaF₃/La₂O₃ was found active even at 873K. At 1023K, the C₂ yield was 12.7% at 49.1% C₂ selectivity. It was found to be stable and had a life-time not less than 50 h at 1023K. The activation energies for CH₄ conversion and C₂ formation at high O₂ 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%LaF₃/La₂O₃ and Au mixed 50mol%LaF₃/La₂O₃ catalysts at 923-1023K. The maximum C₂ yield obtained was 5.4% at 1023K over the 50mol%LaF₃/La₂O₃. The effect of electrochemical oxygen pumping (EOP) on C₂ selectivity and rates of formation of products were studied over both catalysts. Obvious enhancement was observed at 973K over (50mol%LaF₃/La₂O₃)/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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