"Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane"

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Statement of scope and preliminary report

The objective of this program is to investigate the role of metal and oxide catalysts on the selectivity of product composition in partial and full oxidations of methane. Studies of both the gas phase free radical pathways and the surface catalyzed reactions, as well as the interplay of the two, are incorporated in this program, using modern tools of spectroscopic characterization of gas phase intermediates (EPR, optical) and of surface intermediates (Auger/ESCA/EELS). By analyzing the gas phase/surface pathways of methane oxidation, it is hoped that foundations will be laid for the understanding and design of processes for direct methane oxidation to methanol and formaldehyde.

There are five known chemical systems that produce methanol, formaldehyde, or the mixture of the two from methane and an oxidizing gas such as oxygen or nitrous oxide. These comprise:

(i) Homogeneous inverted flames in which methanol is produced by an uncatalyzed free radical reaction between methane and oxygen at temperatures 400-500°C and pressures up to 40 atmospheres;

(ii) Acid zeolites, methane and oxygen which yield formaldehyde at 750°C and subatmospheric pressures;

(iii) Molybdena-derived catalysts, in particular ferrous molybdate, methane, and oxygen, which yield methanol at 450-550°C and 10 atmospheres;

(iv) Molybdena catalysts, methane, and nitrous oxide, which yield methanol and formaldehyde at 500-550°C and subatmospheric pressures;

(v) Supported palladium catalysts, methane, and oxygen, which yield methanol and formaldehyde at 400-500°C and subatmospheric pressures in the presence of chlorine-containing compounds.

In addition, there is a very recent claim that methane can be oxidized to methanol with 92% selectivity at 20-30°C and pressures less than one atmosphere by an aqueous solution of ferric sulfate over a palladium-silver catalyst.

In all the systems producing formaldehyde and methanol from methane except the last one the temperature ranges of the free radical homogeneous oxidation and of the heterogeneously catalyzed oxidation overlap, and it is well known that the heterogeneously catalyzed reactions must be rapidly quenched downstream so that gas phase afterburning does not take place. Our research aims at analyzing separately the gas phase and surface reactions occurring during partial oxidation of methane, and is divided into four tasks:

1. Trapping, Detection, and Identification of Free Radicals. Cryotrap EPR methods, chemical and mass spectrometric methods are being developed and used for the detection of $CH_3\cdot$, $CH_3O_2\cdot$, $CH_3O\cdot$, and other radicals produced during the oxidation of methane.

2. Electron Spectroscopy of Surface Intermediates Auger/ESCA/LEED/TPD. Studies of halogen-treated palladium crystal surfaces have been initiated. A construction of an EELS unit is in design stage.

3. Kinetic and Mechanistic Study of the Catalyzed Combustion of Methane. A quenched recirculating and flow reactor has been constructed for the kinetic studies of methane conversion over polycrystalline supported palladium surfaces.

4. Effects of nitric oxide. These investigations are contemplated for later stages of the project as directed by the results of Task 1-3.

The significance of the mechanistic studies, if successfully concluded, rests in the determination of factors that control the product composition in partial oxidations of natural gas. The ultimate goal is to provide process designers with catalysts and conditions under which methane oxidation can be steered to valuable products such as methanol and formaldehyde or, if desired, to completely clean combustion products, CO_2 and water, free from the oxides of nitrogen.