Direct Catalytic Conversion of Methane to C_2+ Hydrocarbons in Supercritical Water

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Abstract:

Partial oxidation of methane under supercritical water environment at 658 K and 26 MPa using a batch reactor was examined in the presence of metal oxide catalysts and H_2O_2 as a molecular oxygen source. Within a parameter space of feed concentrations (CH_4/H_2O and O_2/CH_4 feed ratios), there existed a domain that gave high C_2-C_4 hydrocarbon yield reaching ca. 4%, with ethane as a major component. Transition metal oxides were active toward C_2+ hydrocarbons production under the present conditions, and the activity was correlated with the surface O1s binding energy.

Keywords: Oxidative methane coupling, supercritical water, C_2+ hydrocarbon production.

1. Introduction

Over the last several decades, extensive research has focused on the direct conversion of methane to oxygenates or higher hydrocarbons. Research in this field has intensified in recent years due to the increased production of methane from shale gas and tight oil.[1] Partial oxidation of methane (POM) apparently possesses process advantages compared to indirect methanol synthesis or Fischer−Tropsch hydrocarbon synthesis, both of which goes through energy intensive synthesis gas (CO + H_2) production route.[2] The conversion of methane to C_2+ hydrocarbons via oxidative coupling of methane (OCM) is a reaction that in principle offers a more energetically favorable pathway.[3] Notwithstanding, it is a challenging reaction due to its required high reaction temperature and high probabilities for secondary reactions, resulting in a tendency toward complete oxidation of reactant methane and its products to CO_2.[4] To mitigate the complete oxidation in the partial oxidation of methane process by lowering the reaction temperature and diluting the reactant-product mixture, the use of supercritical water (SCW) as a reaction media has been attempted.[5] However, the reported work were limited to methanol production, within a limited feed concentration ratio (CH_4/H_2O – O_2/CH_4) parameter space, as shown in Figure 1(a).

In the present study, catalytic SCW-POM using a batch reactor was performed within a parameter space of feed concentrations (CH_4/H_2O and O_2/CH_4 ratios) that has not been explored previously. A domain that indicates high OCM activity was found with unprecedented C_2+ hydrocarbon yield of ca. 4% at a low temperature of 658 K.

2. Experimental

More than 16 catalysts, consisting of transition metal (Fe, Mn, Co, Ni, Ti, La, Cu, Mo, Zn, Al, Ce, W, V and Cr) oxides and activated carbon (AC) were employed. The catalysts were prepared by either an incipient wetness impregnation or co-impregnation method, using water-soluble metal salts, followed by calcination.

Supercritical water-OCM experiments were conducted at 658 K and 26 MPa using a stainless steel batch reactor and H_2O_2 aqueous solution as a molecular O_2 source. Reaction was commenced by immersing the charged reactor into a molten salt bath kept at 673 K, and after designated reaction time (5 min) the reactor was withdrawn and immediately quenched to room temperature under running water. Product gas was retrieved using a gas bag, and the liquid product was collected and filtered with a microfilter. The products were analyzed using two types of gas chromatographs: one with a thermal conductivity detector (TCD) for CH_4, CO_2, H_2, CO, and air quantification, and the other with a flame ionization detector (FID) for

C2+ hydrocarbons (ethane, ethylene, propane, propylene, iso-butane and n-butane) and oxygenate compounds (formaldehyde, acetaldehyde, methanol and ethanol) quantification.

3. Results and discussion

SCW-POM was examined with CH_4/H_2O and O_2/CH_4 feed concentrations as variables. The production of sizable amount of C2+ hydrocarbons, with ethane as a major component, was observed between 0.05 and 0.3 O_2/CH_4 and between 0.03 and 0.4 CH_4/H_2O (Figure 1(b)). In the liquid phase, very small amount (less than 1 %) methanol was the main product, while small amount of propane, iso-butane, H_2, CO, and CO_2 were also detected in the gas phase. All of the metal oxide catalysts tested here were active for the C2+ hydrocarbon production in SCW-POM at the present reaction conditions.
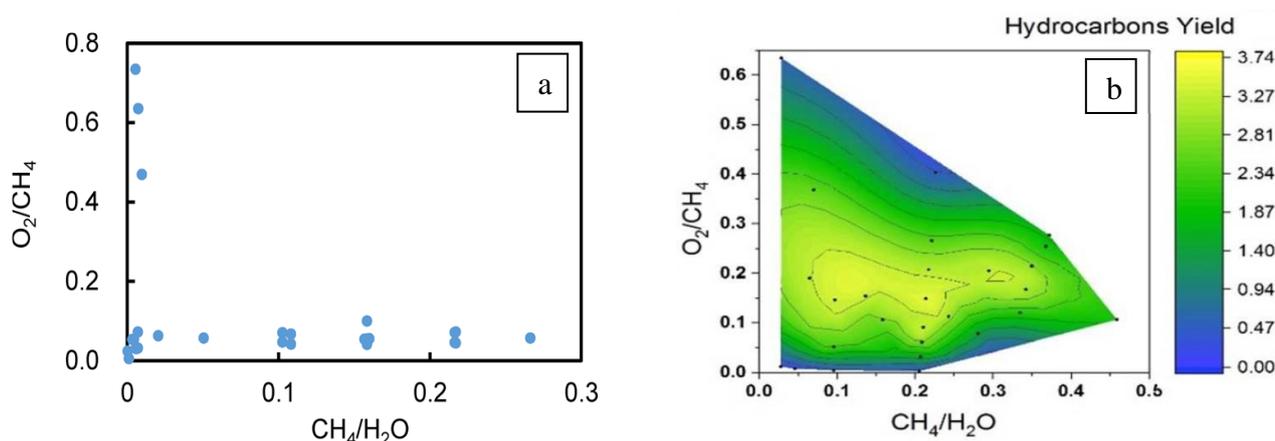
Figure 1. a) Feed gas compositions employed in the preceding SCW-POM studies. b) Hydrocarbon production map with Fe_2O_3 catalyst.

In the high-temperature gas-phase OCM, the C−H bond activation pathways are considered to be mediated by either oxygen species on surfaces or by OH radicals formed via H_2O/O_2 equilibration on catalyst surfaces.[6] This apparently indicates the possibility of catalyst surface (lattice) oxygen participation into the reaction. Thus XPS postreaction analysis of the catalyst surfaces were performed, which showed that the catalysts activity was correlated with the O1s binding energy of one of the surface oxygen species with low O1s binding energy. Detailed data analyses are in progress.

4. Conclusions

The SCW-OCM was performed under SCW environment at 658 K and 26 MPa using a batch reactor. In a CH_4/H_2O−O_2/CH_4 parameter space there existed a domain that exhibit high SCW-OCM activity. Up to C_4 hydrocarbons were produced with ethane as the major component. Transition metal oxides were active catalysts for the SCW-OCM reaction, particularly with low O1s binding energy surface species

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