Methane coupling via catalytically generated OH radicals from H_2O and O_2 using Na based catalysts

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Abstract: Oxidative coupling of methane (OCM) operated with a mixture of methane and oxygen at high temperatures is one of such reactions where C-C bond formation is possible in a single reactor with a mild exotherm. The kinetic measurements using Na_2WO_4 based catalyst indicated a reaction mechanism that was consistent with the OH radical formation from an H_2O-O_2 reaction, followed by C-H activation in CH_4 with an OH radical. A combination of in-situ characterization techniques reveals that molten salt state of Na salt, generating sodium peroxide species on the surface during the high-temperature OCM catalysis.

Keywords: Methane coupling, OH radical, Molten salt.

1. Introduction

Direct synthesis of useful chemicals from methane has attracted significant attention.[1] Oxidative coupling of methane (OCM) operated with a mixture of methane and oxygen at high temperatures is one of such reactions where C-C bond formation is possible in a single reactor with a mild exotherm. The limitation of the reaction partially originates from low attainable yields of C_2 hydrocarbon products and their accurate description based on the reaction mechanism.[2,3] Some catalysts containing alkali metals, such as Na_2WO_4 and Na_2MoO_4 supported on oxides, showed high selectivity towards C_2 products.[4] This contribution discusses evidence of the molten salt state of Na salt during OCM catalysis, which can form OH radicals, using in situ techniques including X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), laser induced fluorescence (LIF) spectrometer, and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS).[5]

2. Experimental

The Na_2WO_4/SiO_2 and Na_2WO_4/TiO_2 catalysts were prepared with a conventional wet impregnation method using $Na_2WO_4\cdot 2H_2O$ (Sigma-Aldrich), SiO_2 (Sigma-Aldrich, Silica Gel, Davisil Grade 646, 35–60 mesh, 300 $m^2\ g^{-1}$) and TiO_2 (Evonik, P25, 50 $m^2\ g^{-1}$). The rates and selectivities of the $CH_4/O_2/H_2O$ reactions were measured using flow reactors and a U-shaped quartz cell (4 mm I.D.) at atmospheric pressure diluted with helium. The reactant and product concentrations were measured using a VARIAN gas chromatograph 450GC with a programmed system that was equipped with a molecular sieve 5 A column, a HayeSep Q column with a thermal conductivity detector and a VARIAN CPWax 52 CB capillary column with a flame ionization detector.

The hydroxyl radicals (OH) formed on the catalyst surface were detected approximately 2 mm above the surface of the alumina boat containing the catalyst. LIF was utilized to detect the formed hydroxyl radicals. The XRD measurement was performed in situ at various temperatures (up to 800°C) under an air atmosphere. The STEM images were recorded using an FEI Titan ChemiSTEM equipped with a Protochips Atmosphere Gas E-cell, where the sample was exposed to 1 atm of air (grade 0.1, ARC3 gas supply) in flowing mode and temperatures between 150°C and 900°C. For AP-XPS, the catalyst sample was loaded on Au foil via a drop-casting method followed by mounting in an in situ reaction cell of an UHV chamber. The reaction cell is integrated with a monochromated Al K-alpha X-ray source and energy analyzer. The sample was heated from room temperature to 800°C under a flow of 0.5 Torr O_2, H_2O, and/or CH_4. All the spectral peaks were calibrated using Au $4f_{7/2}$, whose alignment is supported by the same binding energy of Ti3p of TiO_2 at different experimental conditions after the alignment.

3. Results and discussion

It was found that H_2O, one of the major products, was significantly involved in the conversion of CH_4. The kinetic measurements indicated a reaction mechanism that was consistent with the OH radical formation from an H_2O-O_2 reaction, followed by C-H activation in CH_4 with an OH radical. This rather unrecognized reaction pathway with water is distinctive from the conventional mechanism proposed where CH_4 reacts with active surface oxygen species to generate methyl radicals in the gas phase (Figure 1). It is plausible that the surface active sites that lead to water activation might be different from the ones directly catalyzing CH_4. A combination of in-situ characterization techniques was applied to understand the working state of the catalyst during the reaction. In situ XRD revealed that molten salt state of Na_2WO_4 is prevalent during the catalysis. Successful detection of OH radicals from H_2O and O_2 over the catalyst was achieved using LIF spectroscopy. Moreover, the near-ambient pressure X-ray photoelectron spectroscopy revealed the presence of sodium peroxide species on the surface formed with O_2 at high temperatures. This sodium species is considered to react with H_2O to produce OH radicals. This finding leads to several applications of Na based catalyst, such as selective oxidative dehydrogenation of ethane.[6]

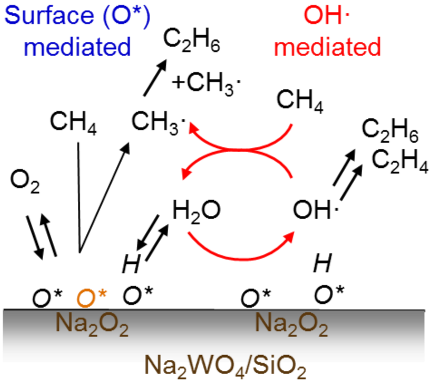

Figure 1. The schematic illustration of radical generation paths using Na_2WO_4/SiO_2 catalyst at high temperature (~800-900 °C) in the stream of $CH_4/O_2/H_2O$ as an example. The molten state Na_2WO_4 at reaction temperature forms quasi-equilibrated Na_2O_2 species, which react with H_2O to generate OH radicals. The OH radical path does not require adsorption of hydrocarbons, thus improving C_2H_4 selectivity in methane coupling.

4. Conclusions

During high-temperature OCM reaction, Na_2WO_4 exhibited molten-salt state covering the surface of oxide support. In the presence of O_2, Na_2O_2 species were generated on the catalyst surface, which react with H_2O to generate OH radicals. This reaction pathway was found responsible for selective OCM because it avoids unwanted ethylene combustion on the catalyst surface. Although further elucidation is necessary to pin down the behavior of active sites and reaction mechanism, this finding opens up new opportunity to selective catalysis of hydrocarbons using OH radicals at high temperatures.

References

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