Radical Initiated Oxidative Conversion of Methane into Methanol over Zero valent catalysts

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Global warming is the greatest problem faced by humankind at the beginning of 21st century. As research be certain of, this global warming is due to emission of carbon dioxide (CO_2), methane (CH_4) and other greenhouse gases. Fueling our current energy demands from fossil fuel is the main reason for these gas emission. As a result, global warming rate is accelerating thereby heating up earth's surface. An alternative way must be established in order to avoid fossil fuel utilization to minimize global warming and associated problems.

Methanol is a well-known fuel source since it is being used in methanol fuel cells, and combustion engines [1]. Methanol is also a main building block for preparation of many organic compounds. It also a best solvent for many reactions. Currently, this fuel being prepared by syngas (CO, CO_2, H_2) conversion by Cu-ZnO/Al_2O_3 catalyst [2]. However utilizing CH_4, a greenhouse gas to synthesis methanol fuel in one step is of great attention since a waste feed stock (CH_4) is being consumed for synthesizing a fuel. This method may also avoid harsh reaction conditions such as high pressure and temperature associated with conventional syngas conversion method.

One step synthesis of methanol from CH_4 has been attempted before with Cu promoted Fe-ZSM-5 catalyst [3]. However conversion and selectivity were poor. High dissociation of CH_4 is a major problem associated with this method which minimizes its conversion at normal conditions. Hence a stable homogeneous reaction system with a different approach to break C-H bond of CH_4 hydrocarbon must be established.

Our approach is to produce methanol by potassium persulfate ($K_2S_2O_8$) generated methyl radicals by means of redox reaction catalyzed by zero valent metals (Fig. 1). Zero valent metals involve in redox reaction with methyl radicals [4]. A water diluted ionic liquid medium was used for reaction in order to boost the reaction by means of stabilizing the radicals. The radicals trapping experiments showed that the $K_2S_2O_8$ and $[BMIM]^+Cl^-$ are essential for this radical reaction to proceed. Oxidative conversion of methane by this system was very effective to produce 530 mg of methanol with just 5 mmol of employed zero valent Cu metal. Generating methyl radical and their successive oxidation to methanol catalyzed by zero valent metals is the efficient method which can be operated at temperature as low as 50 ^{0}C.

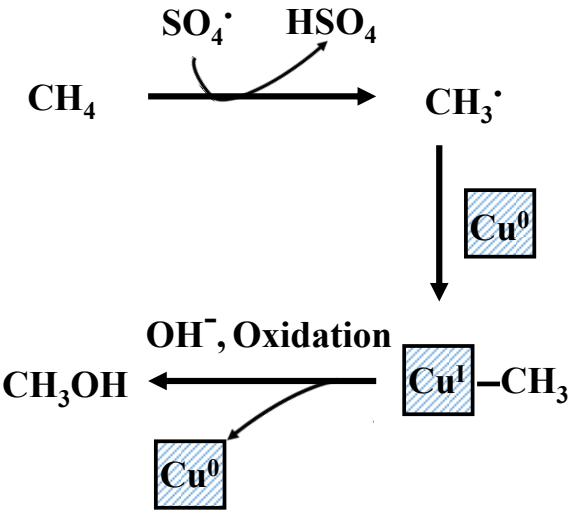

Fig.1 Plausible mechanism of methanol formation by zero valent copper catalyst.

REFERENCES

[1] J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah and G.K. Suryaprakash, J. Am. Chem. Soc., 138 (2016) 778.
[2] K.C. Waugh, Catal. Today, 15 (1992) 51.
[3] C. Hammond, M.M. Forde, M.H. Ab Rahim, A. Thetford, Q. He, R.L. Jenkins, N. Dimitratos, J.A. Lopez-Sanchez, N.F. Dummer, D.M. Murphy, A.F. Carley, S.H. Taylor, D.J. Willock, E.E. Stangland, J. Kang, H. Hagen, C.J. Kiely, G.J. Hutchings, Angew. Chemie Int. Ed., 51 (2012) 5129.
[4] I. Rusonik, H. Polat, H. Cohen and D. Meyerstein, Eur. J. Inorg. Che., (2003) 4227.