Radical-initiated oxidative conversion of methane to methanol over metallic iron and copper catalysts

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ABSTRACT

Oxidative conversion of methane gas into value-added chemicals such as methanol is of great interest due to high economic feasibility of liquid fuel molecules for storage and transportation purpose. Activation and conversion of methane occur at very high temperatures due to its strong C—H bonding and hence the process is highly energy intensive. Therefore, homolytic cleavage of methane to produce CH_3 and H radicals and subsequent conversion to methanol could be an alternative way to catalyze the reaction through a less energy-intensive process. In this work, radical-based conversion of methane to methanol was conducted in water-diluted 1-butyl-3-methylimidazolium chloride ionic liquid (IL) using metallic iron and copper as catalysts. The acidic IL, besides producing the high oxidation potential radicals from $K_2S_2O_8$, enhanced their longevity. ZV Cu was found to be highly active in the reaction catalyzing with steady rate at a lower activation energy ($E_a = 31.5$ kJ/mol) and retains its oxidation state even after the reaction. On the other hand, ZV Fe, catalyzed the reaction with slightly slow initial rate ultimately resulting in moderate activation energy (40.77 kJ/mol). However, it was observed that ZV Fe fails to retain its oxidation state after reaction.

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1. Introduction

Methane, which has been widely used as a power source, is the principal constituent of natural gas. The quality of human life has significantly improved due to methane utilization and as fuel, hence its emissions have been ignored as a significant problem. Methane concentration in the atmosphere, however, has noticeably increased [1–3]. Recently, due to climate change and increasing global warming, methane emission has emerged as a challenging problem [4–6]. Methane, like carbon dioxide is a highly potent greenhouse gas, which contributes one-fifth of the total global warming. It undergoes the infrared radiation absorption-release process that increases the earth's temperature by forming a thermal layer. As such, methane changes the climate by trapping 25 times as much heat as carbon dioxide [7,8]. Hence, effective recycling of methane to synthesize liquid fuels such as methanol is a resolution to circumvent global warming.

Recycling of methane to synthesize methanol is economically important, yet it is highly challenging. A highly active catalyst functions at ambient reaction conditions or low temperature is essential for this reaction in order to proceed. At temperatures greater than the boiling point of methanol (64.7 °C), methane is likely to be over-oxidized, forming CO or CO_2. On the other hand, methane, due to its high C—H bond dissociation energy ($E_{C-H} = 435$ kJ/mol), is a very inactive substrate and is known to be catalyzed by natural enzymes and a few synthetic systems [9–13]. Significant research is yet to be undertaken to invent a system where methane could be oxidized to methanol in a single-step at lower temperatures with high conversion and selectivity.

Although many scientists have addressed the formation of methanol by methane oxidation, the methane conversion was insignificant [14–18]. Another study that performed the methane oxidation using noble metal Pd-, Pt-, and Au-based catalysts has been reported selectivity issue, and demonstrated that the fuel-rich condition is crucial to achieve high methanol selectivity [19]. Conversion and selectivity issues associated with the methane oxidation reaction are due to the high activation energy of the C—H bond of methane, as reported by Wolf et al. [20]. Since the methane oxidation reaction involves the breaking of a C—H bond in its first step, the reaction temperature is supposed to be very high [20], owing to high activation energy, to activate this bond. An alternative way to break this C—H bond at lower temperature remains as a challenge. Homolytic cleavage of CH_4 into CH_3· and H· and the subsequent oxidation of CH_3· are feasible solution to overcome temperature complications. Potassium persulfate ($K_2S_2O_8$) is a potential radical generator that produces SO_4^- radicals with

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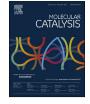*E-mail addresses:* jgseo@mju.ac.kr, jeonggilseo@gmail.com (J.G. Seo).

Table 1
Methane oxidation results obtained over various catalysts under different reaction conditions.

ZV catalyst (mmol)	Missed reaction component	Yield produced (mmol/L)		Selectivity (%)[a]		
		Methanol	Formic acid	Methanol	Formic acid	CH_4 conversion (%)[b]
Cu^0 (0.53)	$K_2S_2O_8$	0.15	–	–	0	negligible
Cu^0 (0.53)	IL	0.25	–	–	0	negligible
–	Cu^0	2.9	2.1	58	42	0.16
Cu^0 (0.53)	none	8.25	5.5	52	48	0.44
Fe^0 (0.53)	none	17	5.6	68	32	0.70
Ni^0 (0.53)	none	9.6	9	41	59	0.60
Co^0 (0.53)	none	2.65	7.3	20	80	0.30
$Cu^{0:}$ Fe:1.4:0.53	none	–	87	0	100	2.80
$Cu^{0:}$ Fe:1.4:1.06	none	–	70	0	100	2.20
$Cu^{0:}$ Fe:1.4:1.59	none	–	46	0	100	1.50
$Cu^{0:}$ Ni:1.4:0.53	none	–	43	0	100	1.40
$Cu^{0:}$ Co:1.4:0.53	none	–	30	0	100	0.80

Reaction conditions: Temperature–60 °C, Pressure–20 bar, $K_2S_2O_8$–0.5 mmol, IL–0.5 mmol.

[a] Selectivity = Moles of target oxygenate/moles of other oxygenates × 100.

[b] CH_4 conversion = Total moles of oxygenates produced/initial moles of CH_4 × 100.

a very high oxidation potential (3.1 V). Previously, $K_2S_2O_8$ was reported to oxidize methane at temperatures as low as 80 °C [21]. Hence, establishing a radical-based mechanism for the methane oxidation reaction would be quite worthwhile.

Metallic catalysts or zero-valent (ZV) metals are highly reactive ingredients in radical-based chemical reactions. They are known to activate persulfate and enhance reactivity when added to a reaction that takes the radical pathway to form products [22]. Hence, the addition of ZV metals as catalysts for methane oxidation by reaction with $K_2S_2O_8$ would maximize the concentration of SO_4^- radicals, which act as a fuel for the reaction to achieve higher conversion of methane. Although radicals are extremely reactive, which is vital to degrading methane, their low stability is always an issue. Radicals need to be stable or possess great longevity that avoids their mutual coupling leading to form unwanted, less oxidation potential radicals. 1-Butyl-3-methylimidazolium chloride ([BMIM]$^+$Cl$^-$), a big and dense IL molecule, is known to form carbine radicals at its acidic proton site [23]. Hence, utilizing denser ionic liquids to increase the longevity of radicals by forming them on a bulkier molecule could allow the reaction to consume the radical fuel efficiently.

In this work, methane oxidation was carried out in a water-diluted IL medium using $K_2S_2O_8$ and ZV metal as oxidizer and catalyst, respectively. The reaction proceeds at a temperature as low as 60 °C to produce concentrated methanol. The methanol formation mechanism was found to be radical-based, confirmed by radical trapping experiments carried out in the presence of CBrCl$_3$ (a radical trapper). ZV metals, when used as a catalyst, were capable of abruptly increasing methane conversion, possibly by maximizing radical fuels. Hence, applying this strategy of using radical fuels to degrade methane to form methanol could further inspire research into methane oxidation.

2. Material and methods

2.1. Materials

Iron powder (99%, <212 µm size), copper powder (99.5%, <425 µm size), cobalt powder (99.9%, <150 µm size), and nickel powder (99.9%, <150 nm) were purchased from Sigma-Aldrich and ground finely prior to use. 1-Butyl-3-methylimidazolium chloride ([BMIM]$^+$Cl$^-$, >98%) and potassium persulfate ($K_2S_2O_8$, 99.0%) were used as obtained from Sigma-Aldrich. High purity methane (99.95%) and carbon dioxide (99.999%) were used for the reactions, and high purity hydrogen (99.99%) was used as standard for gas chromatography (GC) analysis. Double-distilled water was used for all reactions.

2.2. Characterization

Fourier transform infrared (FTIR) spectroscopy was obtained using a Varian 2000 Fourier transform infrared spectrophotometer by accumulating 32 scans between 2000 and 4000 cm^{-1}. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance II+ 400 MHz spectrometer. X-ray diffraction (XRD) spectra were obtained at 2θ between 10 and 90°. A Cu anode was used and continuous scans were taken for each sample. The instrument was operated at a rate of 400 MHz with a spin rate of 13 kHz. Electrospray-ionization mass spectra (ESI–MS) were measured in the range 50–30 m/z with a SYNAPT G2 (Waters, U.K.) instrument. A Perkin-Elmer Lambda 25 ultraviolet-visible (UV–vis) spectrometer was used to analyze samples by absorption spectroscopy in the wavelength range 800–200 nm. High-performance liquid chromatography (HPLC) on an Ultimate 3000 (Dionex, USA) was used to analyze the products in solution. An Aminex 87H (Bio-Rad) column with oven temperature 40 °C and refractive index (RI) (ERC refractoMAX520) detector was used. The eluent was H_2SO_4 (0.01 N) at flow rate 0.5 mL/min. Gas chromatography technique was used to detect gaseous products. The instrument used was Agilent 7890A TCD/FID.

2.3. Catalytic activity tests

A 75 mL reactor fitted with a quartz vessel was used for all the reactions. The quartz vessel was washed with diluted HNO$_3$ before each experiment to avoid any effects of metal impurities on the reaction. In a typical reaction, 20 mL of doubly distilled water was added into the vessel followed by addition of [BMIM]$^+$Cl$^-$ ionic liquid. In order to avoid any unnecessary exothermic side reactions, mixture was cooled in a refrigerator, maintained at 4–5 °C, for 5 min before the addition of $K_2S_2O_8$ (0.5 mmol). The required amount of metallic catalyst was added into the vessel just before fixing it to the reactor. Flushing with nitrogen for 3 min for removal of air from the reaction system. Later, the reactor outlet was closed and methane was purged until 20 bar pressure was obtained inside the reactor. The reactor was covered with a heating jacket. The reaction was carried out for 10 h, unless mentioned, at 60 °C. After the reaction, the heating jacket was removed and the system was allowed to cool naturally; finally, it was ice cooled to condense gaseous products. The gas was released slowly, and a sample was collected in a gas sampler for gas chromatography (GC) analysis. The liquid products were analyzed by HPLC.