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 $CH_3\cdot$ and H· and the subsequent oxidation of $CH_3\cdot$ are feasible solution to overcome temperature complications. Potassium persulfate ($K_2S_2O_8$) is a potential radical generator that produces SO_4^- radicals with

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}. ^{1}H 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.
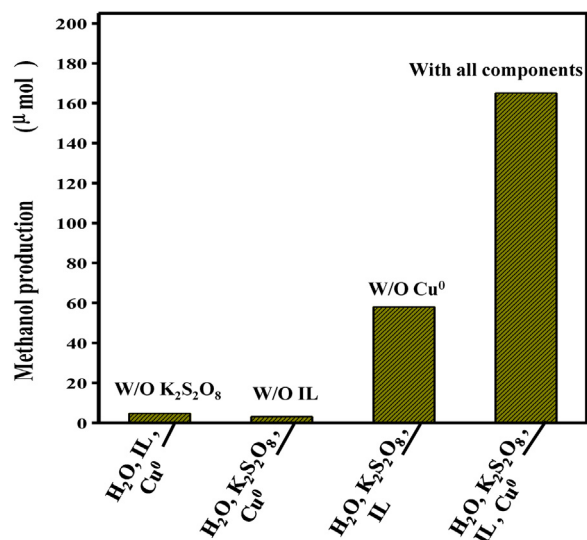
Fig. 1. Importance of different reaction components on methane oxidation reaction (Zv Cu used as catalyst).
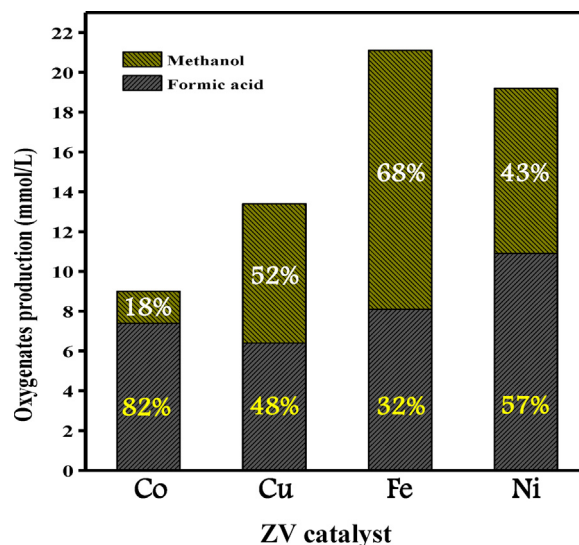

Fig. 3. Activities of different ZV catalysts in the methane oxidation reaction, and their corresponding selectivities towards methanol and formic acid.

3. Results and discussion

3.1. Effect of reaction components on methanol formation

The significance of each reaction component in forming methanol through methane oxidation was understood by carrying out the reactions omitting one component for each time. ZV copper, which is known for radical-based reactions, was employed as a catalyst for all such reactions [24–26]. The methanol produced is specified in Table 1 and graphically represented in Fig. 1. When $K_2S_2O_8$ was omitted from the reaction, methane oxidation was hardly occurred at 60 °C, giving just 5 μmol of methanol in the 20 mL reaction mixture. This observation clearly explains the requirement of a radical generating oxidizer for the reaction to take place, especially at ambient reaction temperature. Further, reaction carried out without IL, i.e. [BMIM]$^+$Cl$^-$, produced 3 μmol of methanol, which is poorer than the former reaction. The instability of highly active SO_4^- radical might be responsible for the lower performance since the unstable radicals are tend to be coupled, producing unwanted H_2 and H_2SO_4 species. When both the IL and

oxidant were tested in the absence of ZV catalyst, the methanol yield was enhanced to 58 μmol. IL enhanced the yield of methanol, which did not occur in the absence of $K_2S_2O_8$, implying a possibility of providing a stabilizing factor for radicals generated by $K_2S_2O_8$. The presence of acidic protons possessed by the IL molecule can also produce more radicals. A complete reaction performed without omitting any of the components produced an abrupt increase in the methanol yield to 165 μmol. The potential of ZV metals is attributed to the enhanced activity observed in the reaction. ZV metals are reported to react with peroxide oxidants [22] by which means they could generate radical fuel in a large quantity inside the reaction system. The radical-rich system could trigger the degradation of an organic molecule such as methane [27], thus forming methanol in great quantity.

The IL ([BMIM]$^+$Cl$^-$) used as water diluted solvent could also degrade by the effect of radical instability during reaction. However, in the current case, [BMIM]$^+$Cl$^-$ was found to be stable as confirmed by ^{1}H NMR (Fig. 2) taken for the system post the reaction. Two additional peaks were observed in the spectra at 2.06 and 3.18 ppm, which are attributed to formic acid and methanol,
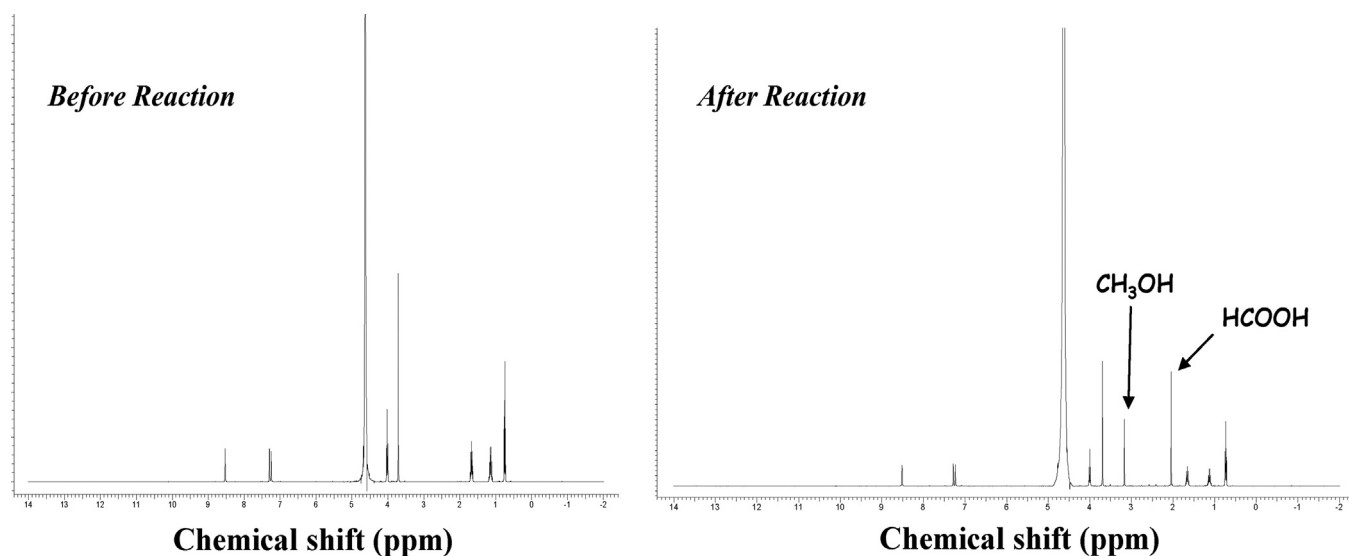

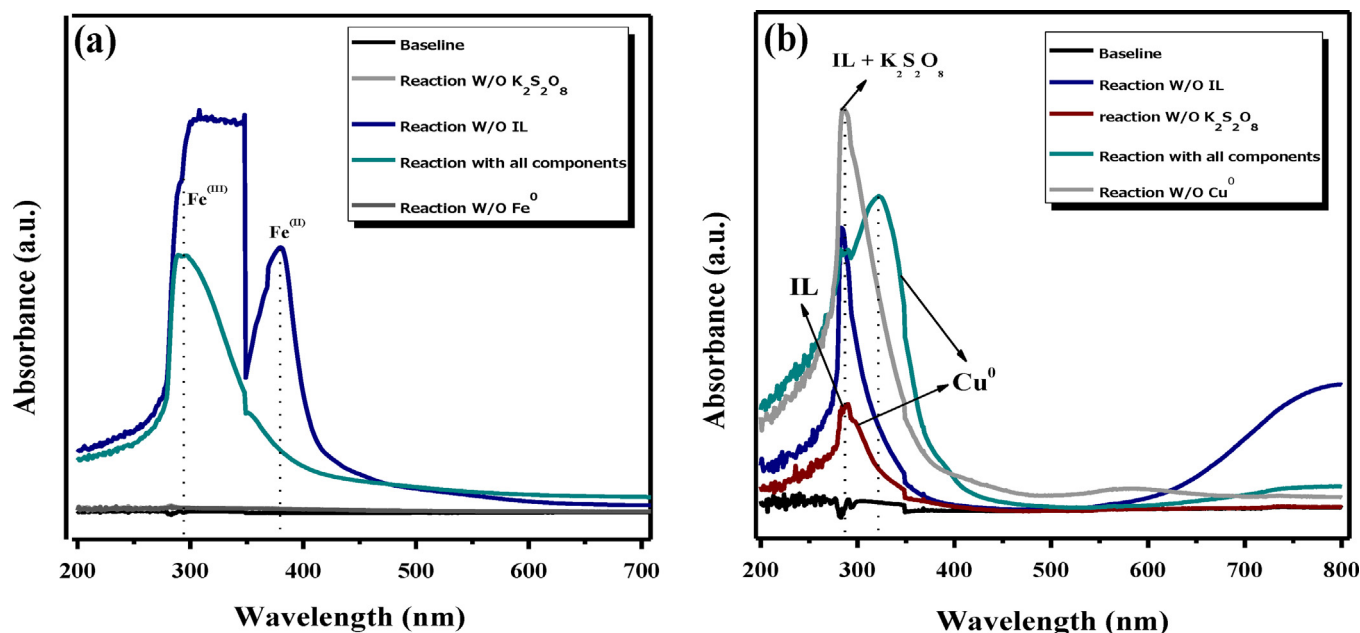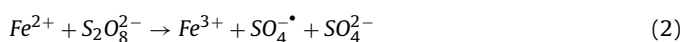Fig. 2. ^{1}H NMR taken before and after reaction for reaction system.

Fig. 4. Absorption spectra taken of reaction systems after the reaction with (a) ZV Fe and (b) ZV Cu.

respectively. No peaks, apart from those corresponding to IL, as a result of impurities formed by the degradation of IL were observed, clearly indicating the stability of [BMIM]$^+$Cl$^-$ against radical instability in the current reaction even at prolonged time.

3.2. Influence of different ZV catalysts on the methane oxidation reaction

Different 3d transition metals were tested as catalysts for the methane oxidation reaction under similar reaction conditions. Fixed moles (0.5) of catalysts was used to run the reactions. The total quantities of oxygenates (methanol and formic acid) produced by different metals are graphically represented in Fig. 3 and tabulated in Table 1. Among the catalysts tested, ZV Fe, which showed the potential to produce 22 mmol/L of the oxygenates was the most active catalyst. This performance was followed by Ni, Cu, and Co metallic catalysts. Fe possesses different stable oxidation states. Each mole of Fe can generate radicals twice by changing the oxidation state from Fe^0 to Fe$^{(II)}$ and further from Fe$^{(II)}$ to Fe$^{(III)}$, as shown in Eqs. (1) and (2) below, and hence exhibited superlative activity. Later, the regenerated SO$_4^-$ radicals react with methane and H$_2$O to produce CH$_3$ and OH radicals, which are subsequently couple up to form methanol as shown in Eqs. (3) and (4).

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{-\bullet} \tag{1}$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{-\bullet} + SO_4^{2-} \tag{2}$$

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^- + OH^\bullet \tag{3}$$

$$CH_3^\bullet + OH^\bullet \rightarrow CH_3OH \tag{4}$$

The percentage yield for methanol and formic acid are emphasized in Fig. 3 so that the selectivities towards different methane oxygenates could be easily understood. ZV Fe gave the highest selectivity (68%) towards methanol among the metallic catalysts tested. ZV Cu was the only other element that showed greater selectivity (52%) for methanol than formic acid, while ZV Ni, Co produced more concentrated formic acid rather than target methanol. Therefore, ZV Fe, Cu (which yielded methanol as a major product) were considered for further studies except while using them as reaction promoters. CO$_2$ is the one of the major gaseous product that forms

in this methane oxidation reaction [15]. However, no CO$_2$ or other gaseous products were detected in this work probably due to high selectivity towards liquid products as a different oxidant K$_2$S$_2$O$_8$ is used in this work unlike to other previous reports those used H$_2$O$_2$ as oxidant [15]. H$_2$O$_2$ used as an oxidant slightly at higher concentration (0.5–1 mmol) is capable of over oxidizing the produced products such as methanol and formic acid. Therefore, at longer times rate of liquid product formation will be slow. The current work K$_2$S$_2$O$_8$ system did not produce CO$_2$ even after 10 h of reaction time and hence it is a meritable method.

3.3. Plausible mechanism of methanol formation over ZV Fe and Cu

The nature of ZV catalysts was studied after the reaction to understand the possible mechanisms for formation of methanol. Both catalysts followed a radical-based mechanism, as confirmed by radical trapping experiments. Bromochloromethane (CBrCl$_3$, a radical trapper) was added in the reaction system. No methanol or formic acid were detected in the HPLC chromatograms taken after reaction. The observation informs that the CBrCl$_3$ dominantly reacts with generated radicals in the system and makes their availability for methane oxidation less. Hence, there was no methanol formation. However, no expected products of trapping experiments (such as CHCl$_3$, CH$_2$Cl$_2$, and CCl$_2$Br$_2$) were observed in the ESI–MS spectrum. The ESI–MS spectrum taken after radical trapping experiments is being shown in Fig. S2. Further, to identify the influence of each reaction component on the radical initiated mechanism, various reactions were carried out by removing one of the components each time and the system after the reaction was analyzed by absorption spectroscopy. The spectra obtained for post-reaction systems of ZV Fe and Cu are given in Fig. 4a and b, respectively. It was observed that the curves for those reactions carried out without ZV Fe and K$_2$S$_2$O$_8$ overlapped with the baseline. This confirms the importance of K$_2$S$_2$O$_8$ in generating radicals in the system. In the case when IL was omitted (only H$_2$O was used as solvent), two broad peaks representing Fe$^{(II)}$ and Fe$^{(III)}$ formation appeared, as shown in Fig. 4a. Eqs. (1) and (2) confirm the methanol formation mechanism by ZV Fe. When all components were retained in the reaction,
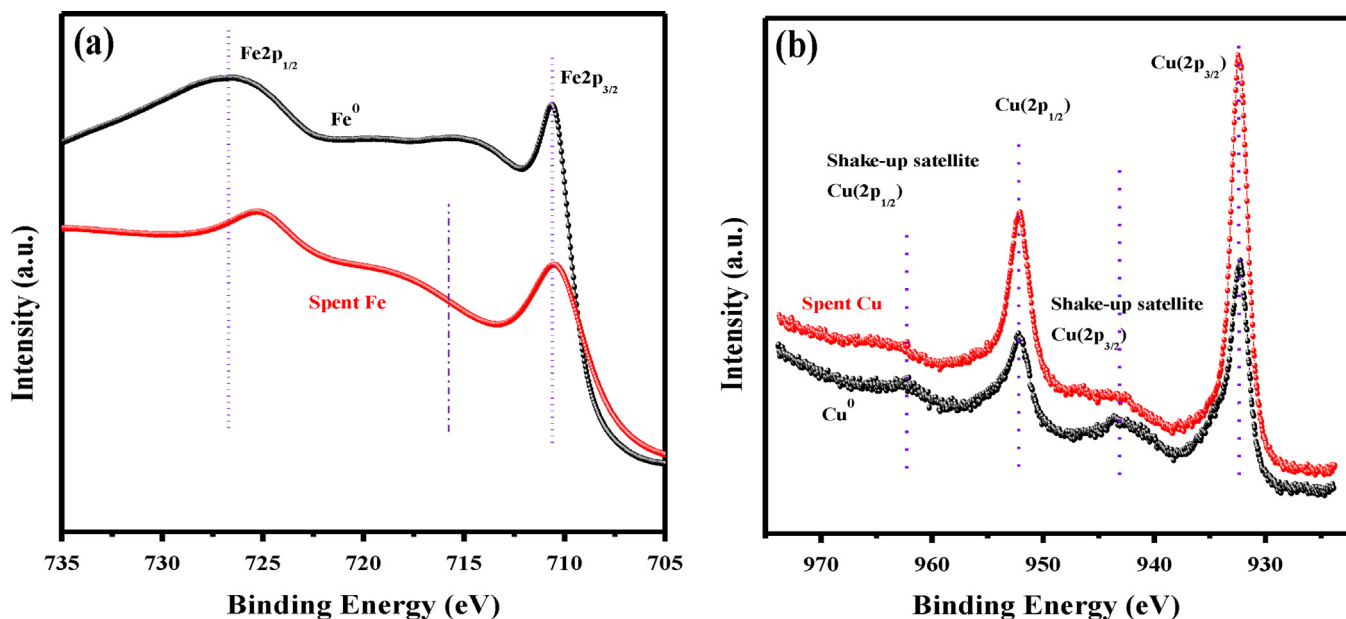
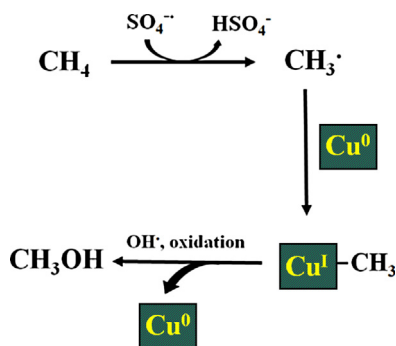**Fig. 5.** High-resolution XPS spectra for (a) ZV Fe and spent Fe and (b) ZV Cu and spent Cu.

Fig. 6. Plausible methane oxidation to methanol mechanism catalyzed by ZV Cu.

only Fe$^{(III)}$ was observed, confirming the successful consumption of ZV Fe.

Unlike Fe, Cu has been reported to retain its metallic properties even after being used to oxidize CH$_3$ radicals [28]. Retention of the Cu oxidation state was further confirmed by UV spectroscopy. Similar reactions as carried out for Fe were performed for Cu. The corresponding UV–vis spectra are depicted in Fig. 4b. A combined peak of K$_2$S$_2$O$_8$ [29] and [BMIM]$^+$ [30] was observed in the spectrum within the range 260–280 nm. The intensities of these peaks, unlike in the Fe system, was very high. Low dispersion of metallic Cu in the system is responsible for such an observation, which could strongly suggest the retention of properties of Cu even after the reaction. The peak at 296 nm is attributed to dispersed metallic Cu in the system [31]. The curve obtained for reaction with all components showed a broad peak at 318 nm, which might be assigned to metallic ZV Cu dispersed at high concentration broadening the peak range. No peak was observed in the range 500–700 nm, suggesting no change in Cu oxidation state during the reactions. Only the experiment omitting IL showed changes in the Cu oxidation state as it possessed an absorption peak at 750 nm. The interaction of Cu with water (solvent) in the absence of IL is responsible for such a peak. The XPS spectra for spent ZV Fe and Cu compared to their precursor forms are represented in Fig. 5a and b. In case of Fe, the peaks were shifted to higher binding energy levels for spent catalyst. Such shifting originates due to the changes in oxidation state. In case of Cu, there were no changes observed in the XPS peak

reflection positions obtained for ZV Cu and Spent Cu. thus, retention of zero oxidation state can be confirmed. The XPS observations are concurring with UV–vis interpretations.

Based on the above observation, it can be concluded that Cu catalyzes a different mechanism to Fe. A plausible cycle of the mechanism is shown in Fig. 6 based on our experimental observations and previous reports [23]. In this mechanism, a methane molecule undergoes homolytic cleavage by a SO$_4$$^-$ radical to form a CH$_3$ radical. The CH$_3$ radical binds to the metallic Cu site thereby changing its oxidation state to Cu$^{(I)}$. In the next step, OH· would be coupled with the methyl group of Cu-CH$_3$ species to produce methanol and reduce Cu$^{(I)}$ back to Cu$^{(0)}$, thereby completing the cycle. Such reaction cyclability of ZV Cu catalyst benefits its reusability in the next batch of reaction (See Fig. S3)

3.4. Effect of catalyst dosage on oxygenate formation

ZV Cu, as mentioned above, possesses a cyclic mechanism. Increase in Cu dosage as a catalyst enriches the radical fuel in the reaction system, which leads to an increase in methanol yield (Fig. 7a). Formation of high concentration of radicals facilitates methane C—H bond activation, thereby reducing the required activation energy [32]. This observation was similar to the quantum chemical analysis of plasma-assisted methane conversion to methanol [32]. The ZV Fe results were different from those of ZV Cu. Increasing the ZV Fe dosage in this diluted IL solvent medium with K$_2$S$_2$O$_8$ as the oxidant did not maximize the methanol yield. This phenomenon might be due to the high potential of ZV Fe to activate K$_2$S$_2$O$_8$ even under normal laboratory conditions. Hence, the radical concentration would be very high before the actual start of the methane activation reaction. The presence of a high number of radicals was reported to cause self-coupling [27] before cleaving methane to form other radicals, as shown in Eqs. (5) and (6), reducing the potential to oxidize methane. Hence, the lower production of methanol is observed.
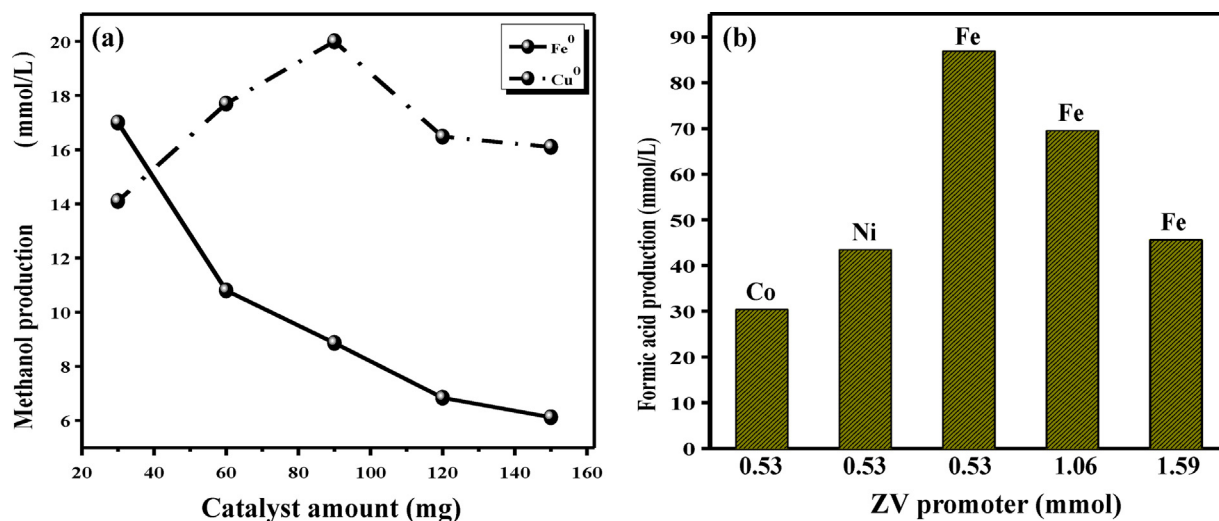
$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^- + OH^\bullet \tag{5}$$

$$OH^\bullet + OH^\bullet \rightarrow HO_2^\bullet \tag{6}$$

Fig. 7. (a) Effect of ZV Fe and ZV Cu catalysts amount on reaction yielding methanol from methane conversion. (b) Consequences of different ZV metals as promoters in methane oxidation reaction (ZV Cu fixed to 1.4 mmol).
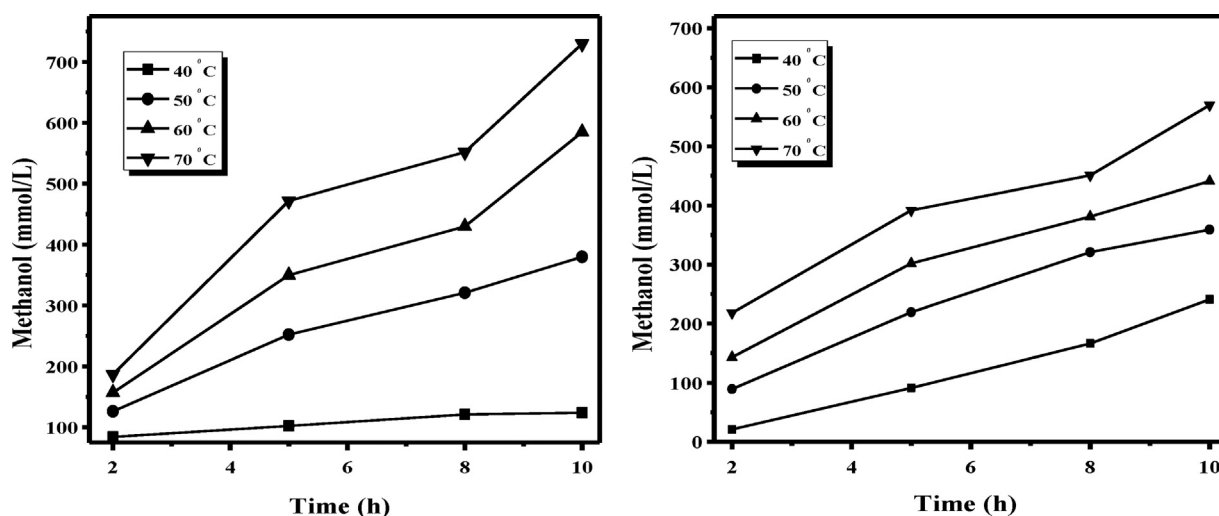

Fig. 8. Effect of temperature on reaction catalyzed by (a) ZV Fe and (b) ZV Cu (Note: moles of Fe and Cu were fixed to compare activation energies).

3.5. Consequences of different ZV metals employed as promoters with metallic Cu as catalyst

To understand the effect of mixed ZV catalysts, several experiments were carried out fixing the ZV Cu moles (1.4 mmol) and varying the ZV Fe moles. ZV Ni and Co were also tested as promoters. The results are depicted in Fig. 7b and Table 1. Mixed ZV catalysts greatly stimulated the methane conversion and produced a high concentration of oxygenates in the reaction system. Formic acid, which is an over-oxidized product of methanol, was the only product obtained in these experiments. Hence, there must be two reactions occurring simultaneously: methane conversion to methanol and its over-oxidation. When mixed ZV metal catalyzes the reaction, the probability is one of the ZV metals actively involves in the later reaction and completely over-oxidizes the methanol formed. Further, the yield formation tendency was in line with earlier results. Lower moles of the Fe promoter correlated with increased formic acid yield. When 0.53 mmol of ZV Fe added as promoter, 82 mmol/L of oxygenate (formic acid) was produced; this was four times superior performance when compared to that of without ZV Fe.

3.6. Effect of temperature on ZV Fe and Cu-catalyzed reactions

The responses of the reaction at different temperatures were studied for ZV Fe and Cu fixing the amount of catalyst at 0.53 mmol. The catalytic experiments were carriedout at 40, 50, 60, and 70 °C. As the resulting product ie., methanol evaporate beyond 70 °C, the studied temperature range was below 70 °C. Temperatures below 40 °C are ignored as are expected to be incapable to activate strong C—H bond of methane. As expected, the results demonstrated that, the yield of methanol increased with increasing temperature for both ZV Fe and ZV Cu (Fig. 8a and b). However, the increment in the yield was rapid in the case of ZV Fe. There was no much difference in the methanol quantity at initial hours of reaction signifying slow initial rate of reaction. However, with further progress in the reaction, appreciable amount of methanol quantity could be obtained. Among the studied catalysts, Fe catalyzed reaction possess faster kinetics at later hours but the rate found to be steady for ZV Cu. There was a rise in reaction rate from 40 to 70 °C in case of ZV Fe. At higher temperatures (50–70 °C), methanol yield production was found to be maximum within first 5 h. Subsequently, methanol accumulation rate in the reaction system was low. Either inacces-
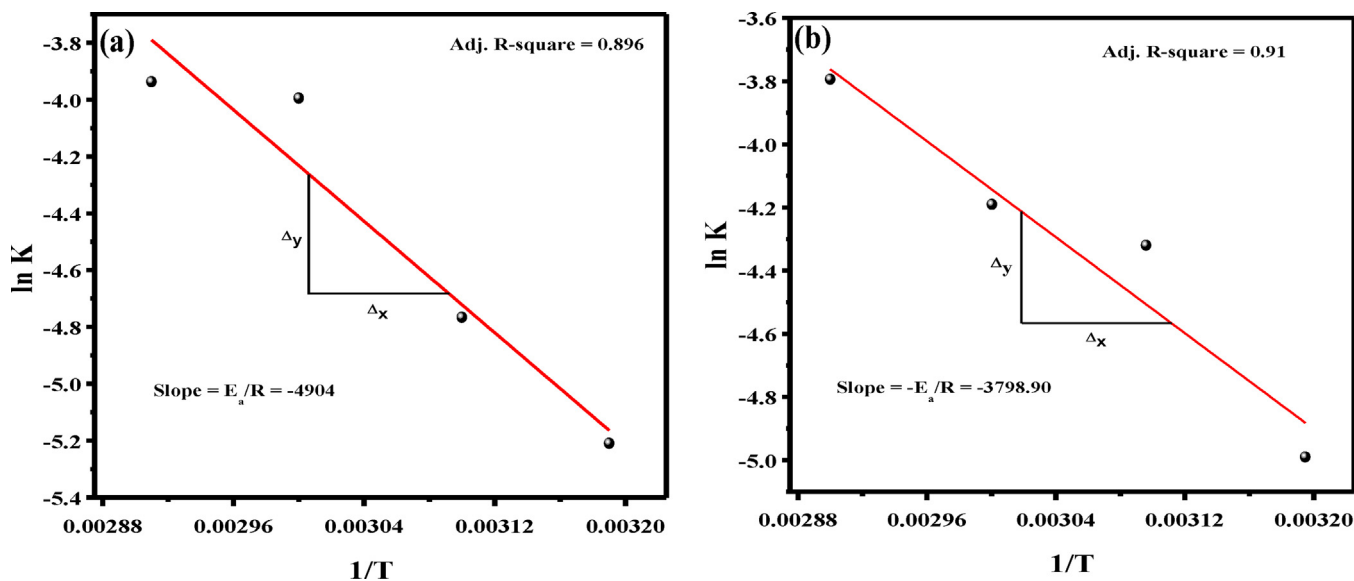
Fig. 9. Arrhenius plot obtained for methanol formation in the reactions catalyzed by (a) ZV Fe and (b) ZV Cu.

sibility of radicals to activate methane at longer reaction times or the over-oxidation of methanol to produce formic acid with time is responsible for this behavior.

3.7. Activation energy

Temperature-dependent experiments helped to calculate activation energy (E_a) needed for methanol formation, over ZV Fe and Cu using the Arrhenius equation (Eq. (7)).

$$k = A \cdot e^{-Ea/RT} \tag{7}$$

where k is the rate of methanol formation (mol/L), A is the pre-exponential rate, E_a is the activation energy (kJ/mol), R is the rate constant (8.314 J/mol/K), and T is temperature (K) of the reaction system. The Arrhenius plots (ln K vs. 1/T) for ZV Fe and Cu are shown in Fig. 9a and b. respectivwly. E_a calculated from the slope was found to be 31.5 kJ/mol for ZV Fe and 40.77 kJ/mol for ZV Cu. Although there are few reports on E_a of methanol production from methane, the energies obtained in this work are decent as the rate of the reaction solely depends on radicals generated and not on other properties such as high surface area and greater acidity associated with heterogeneous catalysts.

4. Conclusions

Methane oxidation was carried out over various ZV catalysts. A radical pathway for methane degradation and methanol formation is proposed. Water-diluted 1-butyl-3-methylimidazolium chloride medium was found to produce more methanol. The presence of acidic protons in IL is responsible for SO4- radical production in a large concentration, which in turn oxidizes greater moles of methane. The higher density and bulkier moiety of IL also assists in maximizing the radicals' longevity. The ZV catalysts showed a tendency to abruptly increase methane conversion and methanol formation by complimenting the radical-based reaction. ZV Fe is found to be the best candidate in present study with higher efficiency as it involves twice in the reaction mechanism yielding high concentrated methanol with 68% selectivity. Though, ZV Cu shows low activation energy (Ea = 31.5 kJ/mol) for methanol formation but possess lower selectivity corresponding to 52%. ZV Cu retained its oxidation state after reaction. On the other hand, ZV Fe, with moderate selectivity, found to possess a higher activation

energy (Ea = 40.77 kJ/mol) than that of ZV Cu. ZV Fe did not retain its oxidation state after reaction.

Positive perseverance of Cu in retaining its oxidation state may motivate further research to enhance methanol yield by means of designing heterogeneous catalysts incorporating metallic Cu on reaction boosting supports.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2017.12.001.

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