One Step Acetic Acid Formation Through Simultaneous Activation of Methane and CO\textsubscript{2} over Cu Exchanged Zsm-5 Catalysts

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Abstract

The ultimate goal of our study is the development of strategies to exploit methane and carbon dioxide resources more efficiently and cleanly. Due to the high stabilities of both methane and CO\textsubscript{2}, simultaneous C-H bond activation of methane and CO\textsubscript{2} is the one of the toughest challenge in catalysis. Formation of acetic acid was achieved by the concurrent feed of methane and carbon dioxide over Cu loaded basic cation ZSM-5 catalysts under the continuous flow microreactor system. The formation of acetic acid was observed in the broad temperature range of 425°C to 525°C with a co-feed unimolar ratio of CO\textsubscript{2}/CH\textsubscript{4}, under low space velocity of 360 ml hr\textsuperscript{-1} based on methane. The formation rate of acetic acid was observed to be low in Cu\textsuperscript{0}-H-ZSM-5, however, the cation exchanged M\textsuperscript{+}-ZSM-5 catalyst showed remarkable increment in the formation rate of acetic acid. The basic cations showed the catalytic activity in the following order K>Na>Ca>Li. This indicates that basic cations helps in providing surface active CO\textsubscript{2} in the form of carbonates, which led to efficient CO\textsubscript{2} insertion into activated C-H bond from methane over reduced Cu metallic nanoparticles. The bi-functional Cu and basic cationic species, together ascribes to the outstanding formation rates of acetic acid. The Cu\textsuperscript{0}-K-ZSM-5 catalyst exhibited the highest formation rate of acetic acid of 12424 μ mole gcat\textsuperscript{-1}h\textsuperscript{-1} at the initial activity and 395 μ mole gcat\textsuperscript{-1}h\textsuperscript{-1} at steady state, for 10 h time-on-stream at 500°C.

Keywords: Co-activation of CH\textsubscript{4} and CO\textsubscript{2}; Acetic acid; Cu\textsuperscript{0}-K-ZSM-5; Continuous system
Introduction

Valuable chemicals from abundant resources, which are global warming gases like methane and CO$_2$, evoke great attention not only from the viewpoints of both energy and environmental issues, but also due to its potential utilization as an alternative and economical feedstock [1-4]. For the conversions of methane and CO$_2$, surface activation using heterogeneous catalyst has been proposed as one of the plausible ways to overcome very high thermodynamic and kinetical barriers [5] due to their high stabilities and chemical inertness [6]. Moreover, the simultaneous activation of both molecules looks attractive but even tougher [7]. C-H bond activation of methane has been applied to give aromatics, olefins, and oxygenates through the non-oxidative or oxidative conditions with the help of oxidants [8] by loosening or dissociating of C-H bond of methane [9]. And CO$_2$ activation has been believed to need a reductant to lose oxygen or at least should be activated molecularly with the help of metallic Lewis acid sites or basic sites [10]. Even though simultaneous activation of methane and CO$_2$ seems to be very difficult [11], there have been reported such as CO$_2$ (dry) reforming of methane to synthesis gas [12] and oxidative coupling of methane with CO$_2$ at high temperature, but quite less on oxidative conversion of methane into methanol with CO$_2$ and/or CO, and carboxylation of methane to acetic acid as an insertion of CO$_2$ into C-H bond of methane [13].

When it comes to the acetic acid, the most prevailed acetic acid manufacturing process is methanol carbonylation process, which has three steps starting from methane to methanol via synthesis gas followed carbonylation with CO homogeneous conditions over catalyst system such as rhodium and iridium complexes with HI [14] among (1) carbonylation of methanol; (2) isomerization of methyl formate; (3) syngas to acetic acid; and (4) vapor phase oxidation of ethylene etc. So, the direct one-step formation of acetic acid via the carboxylation of methane with CO$_2$ evokes great interest but very challengeable for simultaneous activation of both reactant molecules and overcoming thermodynamic barrier. Also, there was no loss of any
atoms after the reaction. So, the simultaneous activation of these two molecules on the same catalyst system for forming acetic acid is subjected to have great merits comparing to current major acetic acid processes.

Despite of this advantage, the simultaneous conversions of methane and CO₂ was hardly achieved, mainly due to thermodynamic unfavourability in terms of free energy [5]. There were several trials to get over thermodynamic unfavourability by adding O₂[15], and dielectric barrier discharge [13]. Acetic acid from CH₄ and CO₂ was firstly reported by Pd/Cu complexes [15] in CF₃COOH solvent and K₂S₂O₈ (15 mol%) acts as an oxidizing agent homogeneously, which furnished 7% yield on acetic acid. However, it was explained later that no CO₂ participated but CF₃COOH acted as a carboxylate source due to more thermodynamically favorable reaction between CH₄ and CF₃COOH. Heterogeneous approaches mostly have adopted the two-step, stepwise, periodic or cyclic reaction modes by using Co-Cu, V₂O₅-PdCl₂/Al₂O₃, Pd and Rh/TiO₂, Pd and Rh/SiO₂, Pd/C and Pt/alumina [18] as catalysts with less than 45 μ mole gcat⁻¹ h⁻¹ of formation rate and low selectivity as well. Huang et al. proposed two-step process for the synthesis of acetic acid over bimetallic Co-Cu catalysts by alternative feeding of CO₂ and CH₄ with H₂ sweeping between the cycles to give various oxygenates including poor acetic acid selectivity, wherein the first step formation of surface carbonaceous species took place via the dissociation of methane over Co to give Co-CH₃ species, then CH₃ inturn produced CH₃-Cu species which rearranged to metal-O-C-O-CH₃ followed by addition of hydrogen to give acetic acid [19].

However, a couple of theoretical and spectroscopic studies have shown the possibility of the direct conversion of CH₄ and CO₂ to acetic acid using heterogeneous catalysts. Liu et al. demonstrated the route via CO₂ thermodynamically favoured than the route of CO, which could be formed by dielectric-barrier discharge [20]. Zhang et al. proposed a two-step technology but only by the DFT studies, by showing the conversion of both CH₄ and CO₂ directly to acetic acid at low temperature (100°C to 400°C) over Cu (111) surface and proposed the Eley-Rideal mechanism between the gaseous CO₂ and metal-CH₄, which was formed dehydrogenation of CH₄ on metals by the first-principle DFT-GGA calculations [21]. Recently, Limtrakul et al. proposed the concerted bifunctional mechanism by the DFT (M06-L) over Au(I)-exchanged ZSM-5 zeolite, which draw out the metal-Broensted acid synergistic effect on the activation of CH₄ and CO₂ by the homolytic dissociation of CH₄ followed by the insertion of CO₂ activated on B-sites [6].

However, Spivey et al. reported the formation of acetate as an intermediate from 50% CO₂/50% CH₄ mixture over 5% Pd supported carbon and Pt supported alumina catalysts by using (DRIFTS) [18]. Zhu et al. confirmed by FTIR the formation of CH₄ and CH₂O species over Cu/Co supported oxide catalysts [22]. Recently, a new strategy was investigated using C¹³-NMR for co-conversion of CH₄ and CO₂ over Zn/H-ZSM-5 catalyst. Where, the zinc sites were observed to effectively activate CH₄ to form (-Zn-CH₃), followed by the insertion of CO₂ into the Zn-CH₃ to form zinc acetate species [23]. Ding et al. investigated and confirmed the effectiveness of Pd/SiO₂ and Rd/SiO₂ in this carboxylation reaction by step-wise isothermal routs [17]. Narsimhan et al. reported the mechanistic studies for direct conversion of CH₄ and CO₂ onto acetic acid using Cu-exchanged zeolites (ZSM-5 and MOR.) [24]. Wannakao et al. illustrated the possibility of methane and CO₂ activation and their corresponding adsorption capacity over some metal ion exchanged zeolites [25].

However, to the best of our knowledge, there is no report which deals with the experimental study for the direct synthesis of acetic acid from CH₄ and CO₂ under continuous fixed-bed reactor using concurrent feeding. In this work, we reported the use
of copper and basic cation-loaded ZSM-5 catalyst for the direct synthesis of acetic acid from CO₂ and CH₄ under continuous fixed-bed reactor after reduced with H₂ in a reactor before reaction. So, we presumed the role of metallic Cu species and the basic cations as a bifunctional catalyst for the simultaneous activation of CH₄ and CO₂ which enabled the continuous formation of acetic acid.

**Experimental**

**Ion-exchanged Cu-ZSM-5 preparation**

Commercial H-ZSM-5 procured from (Zeolyst) was cation-exchanged three times using 0.1 M of LiNO₃, NaNO₃, KNO₃, and Ca(NO₃)₂ and then calcined at 500°C for 5 h. The prepared M⁺-ZSM-5 was then ion exchanged with 0.25 M of Cu(NO₃)₂·3H₂O. In a typical synthesis procedure 1 g of M⁺-ZSM-5 was charged into 50 ml round bottom flask with a certain amount of Cu(NO₃)₂·3H₂O and refluxed at 60°C for 6 h. The solid was then filtered and washed several times with de-ionized water dried and calcined at 550°C for 5 h.

**Catalytic activity**

The direct reaction between CH₄ and CO₂ was carried out in stainless fixed-bed reactor loaded with appropriate amount of catalyst (300 mg) and was subjected to He flow (30 ml/min) for 20 min at room temperature to remove the air. Subsequently, He flow was switched to hydrogen (5 ml/min) and the catalyst was reduced at 450°C for 2 h. The reduction was carried out using a temperature program from 30°C to 400°C in 30 min and then the temperature was raised to 450°C in 30 min and maintained for 2 h. Then the desired temperature for the reaction was adjusted under hydrogen flow 2 ml/min. After the reduction, at the desired temperature hydrogen flow was switched to a mixture of 1% CH₄ in He (1.5 ml/min) and CO₂ (1.5 ml/min) simultaneously. The reaction was conducted at different temperature ranges from 425°C to 525°C. The products were analyzed by online gas chromatography (Younglin Instrument, Acme 6000 series, Korea) equipped with FID and TCD.

**Characterization of the catalysts**

Powder X-ray diffraction patterns (XRD) of catalysts were obtained using Rigaku Miniflex X-ray diffractometer with CuKα radiation source (λ=0.154 nm) at 30 kV, 15 mA from 5° to 90°. UV-vis-NIR diffuse reflectance spectra (DRS) were performed with a Shimadzu UV-2501PC spectrophotometer equipped with a reflectance attachment and BaSO₄ was used as the reference material. The NIR spectra were recorded in the reflectance mode at room temperature. The FTIR spectra were recorded using a Nicolet Impact 410 spectrometer over a range of 400 cm⁻¹ to 4000 cm⁻¹. The X-ray photoelectron spectra were obtained using an ESCALAB MK II spectrometer provided with a hemispherical electron analyzer and Al anode X-ray exciting source (Al Kα=1487.6 eV). TEM images of the samples were recorded on a JEOL JEM-2100 (Japan) operating at 200 kV. Temperature-programmed reduction (TPR) of the catalysts with hydrogen (5 vol.% H₂ in helium) was performed from 50°C to 600°C with heating rate of 10°C/min in a conventional flow system equipped with a TCD detector for monitoring of the H₂ consumption.

**Results and Discussion**

**Screening the catalytic performance different temperature and the molar ratios of methane and CO₂**

FIG. 1 depicts the rates of acetic acid formation depending on temperature: the initial activity within 21 min. (a); till 1 hr after 21 min. (b); and hourly activities at 500°C (c); and dependency of CH₄ to CO₂ ratios over Cu⁰-Na-ZSM-5 catalyst (d). The
catalytic activity was tested between 425°C to 525°C. The activities towards the formation of acetic acid increased with temperatures. The highest activity was observed at 525°C about 50 mmole g<sub>cat</sub>-1 h<sup>-1</sup> at the first run but rapidly decayed compared to that at 500°C. Interestingly steady formation of acetic acid was observed with the highest at 500°C for 10 h of time-on-stream. Since acetic acid formation is directly dependent on the molar ratios of methane and CO<sub>2</sub>, thus the flow optimization was carried out as shown in FIG. 1d and the equimolar ratio 1:1 of methane and CO<sub>2</sub> showed the highest rate of formation of acetic acid at 500°C.

FIG. 1. Acetic acid formation rates on the reaction time over Cu<sup>0</sup>-Na-ZSM-5; initial activities for 21 min (a); and activities from 24 min till 1 h (b) at different temperatures; acetic acid formation rates for 10 h at 500°C (c); and effect of CH<sub>4</sub>/CO<sub>2</sub> molar ratios on the formation of acetic acid at 500°C (d).

Effect of basic cations: In order to know the role of basic cations in Cu<sup>0</sup>-M-ZSM-5 catalysts (M=Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>), their activities were compared with Cu<sup>0</sup>-H-ZSM-5 (FIG. 2) at the initial 9<sup>th</sup> min (FIG. 2a), 1 h (FIG. 2c) and 10 h (FIG. 2d) time-on-stream after the initial 1 h acetic acid was the only product obtained. So, FIG. 2b showed the product distributions which gave formic acid and methanol only at the initial period of 9<sup>th</sup> min. For the whole range of reaction temperatures, Cu<sup>0</sup>-H-ZSM-5 catalyst gave poor activities than any other basic cation exchanged Cu<sup>0</sup>-M-ZSM-5 catalysts. Cu-K-ZSM-5 catalyst gave the highest activity (395 μ mol. g<sup>-1</sup> h<sup>-1</sup>) for 10 h after one hour of drastic decrease. Even the Cu-Na-ZSM-5 catalyst gave the highest formation rate at the initial period but showed more drastic decline after 24 min than Cu-K-ZSM-5. This indicates that the activation of CO<sub>2</sub> is closely related to the alkali cations, which helps to insert onto C-H activated species from methane. The higher CO<sub>2</sub> adsorption capacity in K-ZSM5 is attributed to the acid-base interaction between framework and
CO$_2$ molecules. The CO$_2$-TPD of the catalysts which Cu-K-ZSM5 exhibited the highest concentration of adsorbed CO$_2$ among all of the prepared catalysts (FIG. S1$^\dagger$). So, the effective charge density of the cations inside the zeolite pores is assumed to be the reason for higher CO$_2$ adsorption. The CO$_2$ adsorption capacity slightly increases with the cation size as follow Li$<$Na$<$K. The population of divalent cation at the pore entrance of zeolite framework is less and has an only half number of cation than that of monovalent exchanged ZSM-5, which explains the low activity in Ca-exchanged ZSM-5 catalyst [26]. The experimental results were observed to match reasonably with the above explanation (FIG. 2).

![FIG. 2. Methane conversion and acetic acid formation rate over different cation exchanged Cu-Na-ZSM-5 catalysts at 500°C; methane conversion and acetic acid yields (a); and product distribution in liquid products (b); at 9$^{th}$ min of time-on-stream; methane conversions and acetic acid yields at 1 h (c); and after 10 h of time-on-stream (d).](imageurl)

**Effect of catalyst regeneration:** The regeneration studies were performed in the cases of Cu-Na-ZSM-5 and Cu-K-ZSM-5 catalysts. The used catalysts after 10 h of reaction were calcined at 550°C for 5 h in the muffle furnace and tested for another 10 h as shown in TABLES. S1-S3$^\dagger$. The regenerated catalysts showed comparable activities to those of fresh catalysts (~70% in terms of formation rate of acetic acid). The activities of both fresh and regenerated catalysts (FIG. S2$^\dagger$) showed a steady decline in the catalytic activity, aggregation of the Cu$^0$ nanoparticles was suspected to be the reason for deactivation. The
aggregation, in turn, increased the Cu sizes and thus diminishing the effective Cu\(^0\) nanoparticles of appropriate sizes for methane activation [27].

FIG. 3a shows plots of the methane conversions and acetic acid selectivity over Cu-M-ZSM-5 catalysts with the different exchanged cations. Methane conversion decreased significantly for all of the catalysts after 20 min by the rapid agglomeration of Cu under the reductive environment due to methane activation as CH\(_3\)-H.

![Graph showing methane conversion and acetic acid selectivity over different cations exchanger Cu\(^0\)-M-ZSM5.]

**FIG. 3.** Methane conversion and acetic acid selectivity over different cations exchanger Cu\(^0\)-M-ZSM5.

**XPS analysis:** XPS analysis of calcined Cu-Na-ZSM-5 showed the presence of peak corresponding to Cu\(2p^{3/2}\) at 933.9 eV, the evidence of shakeup peak at 943.9 eV indicating the presence of Cu (II) and at 932.4 eV which could be due to Cu\(^+\) or Cu\(^0\) in FIG 4a [28]. Practically in the calcined catalyst, the existence of Cu\(^0\) species could be hardly possible. So, it’s better to consider that the calcined Cu-Na-ZSM-5 consisted of Cu\(^{2+}\) and Cu\(^+\). XPS of the reduced Cu-Na-ZSM-5 in FIG. 4c also showed two peaks at 933.9 eV and at 932.4 eV. The peak at 932.4 eV is comparatively higher compared to the freshly calcined catalyst since the catalyst was reduced by hydrogen so the major peak could be assigned as Cu\(^{1+}\) or Cu\(^0\) species and it is assumed that the reduced catalyst was rich in Cu\(^0\) species. Also, XPS of the used Cu-Na-ZSM-5 in FIG 4b catalyst showed a decrease in the intensity of the peak at 932.4 eV.
FIG. 4. XPS and XRD results of Cu-ZSM-5: XPS of fresh calcined Cu-ZSM-5 (a); used Cu-ZSM-5 (b); and reduced Cu-ZSM5 (c); XRD of calcined Cu-ZSM-5, reduced Cu-ZSM-5 and used Cu-ZSM-5 (e&f).

**XRD pattern:** XRD analysis was carried out on the three catalysts: calcined, reduced and used Cu-Na-ZSM-5. XRD shows the typical diffraction peaks at 2θ=7.94°, 8.85°, 14.90°, 23.33°, 23.90° and 24.50° which are characteristic to the parent ZSM-5 [29]. FIG. 4f shows the XRD patterns of the fresh reduced and used catalyst. The reduced catalyst showed the existence of Cu⁰ species confirmed at 2θ, 43° and 51° which corresponds to the lattice planes of the cubic copper phase (111) and (200), respectively [30]. These peaks were also observed in the case of used catalyst. Thus, based on the XRD and XPS analyses the certain sized Cu⁰ species would be responsible or direct formation of acetic acid from CH₄ and CO₂ together with basic cation in ZSM-5.

**EPR and UV-vis-NIR analysis:** EPR and UV-vis-NIR spectra of the calcined Cu-Na-ZSM-5 catalyst are telling the presence of the isolated Cu²⁺ ions with tetragonally distorted octahedral coordination. In EPR spectrum, typical Cu²⁺ ion species having axial anisotropy of g factors with parameters g‖=2.33, A=137 G, g⊥=2.054 (FIG. 5a) and large absorption band in the range of 500 nm to 1400 nm centred at 800 nm was observed in (FIG. S3†). The broad transition band at ca. 600 nm - 850 nm in UV, which corresponds to d-d transition 2T₂g ← 2E_g, which is inherent of Cu²⁺ ions in zeolites [31]. An intense peak at 250 nm can be assigned to the O₂⁻ → Cu²⁺ charge transfer transition. And additional peak closed to 365 nm was observed. They are related to d-d transitions of Cu (II) species. The spectrum of these conditions is in agreement with the reported in the literature for comparative specimens and relates to Cu (II) in zeolitic cavities [32]. As shown in the EPR (FIG. 5b) spectroscopy, the adsorption of methane over calcined catalysts have comparably small amounts of isolated Cu²⁺ O₆ ions. The EPR spectrum having axial anisotropy of g factors with parameters g‖=2.31, A=150 G, g⊥=2.051, EPR signal intensity and area shows that the amounts of isolated copper ions Cu²⁺ O₆ decreased with methane adsorption, which means the methane reduces Cu²⁺ species to Cu¹⁺ and Cu⁰ by the hydrogen species which were induced through the dissociative
activation of methane. This is also reflected in the case of UV-vis DR after adsorption of methane. When the calcined sample was reduced with hydrogen at 450°C, the “d-d” transitions of Cu^2+ ions in the range of 500 nm to 1400 nm was not visible on the spectrum, as a result of this treatment, the reduction of Cu^2+ ions happened. The H₂ treated Cu-Na-ZSM-5 exhibited different line shapes at 230 nm, 314 nm, and 560 nm. The first band showed at 230 nm corresponding to Cu^{1+}, and plain to see the band at 560 nm in the reduced catalyst is assigned to Cu° and this peak was also observed to be increased after introducing CH₄/CO₂. The transition appearing at 314 nm upon reduction at 450°C is assigned to the internally allowed transition 3d¹⁰⁴s → 3d¹⁰⁴f of isolated copper atoms of Cu⁰ [33]. These phenomena can be assigned to the aggregation of Cu⁰ [34]. This drastic decrease in the intensity of the hyperfine splitting of Cu^2+ was also confirmed by the in-situ EPR by the intrusion of methane over calcined Cu-Na-ZSM-5 catalyst.

FIG. 5. In-situ EPR of calcined, reduced, and after introducing of methane and CO₂ over Cu-Na-ZSM-5 (a); calcined and methane intrusion at 450°C onto the calcined Cu-Na-ZSM-5 (b).

In-situ FT-IR spectra: In-situ FT-IR studies were carried out to elucidate the reaction mechanism over reduced Cu-Na-ZSM-5 catalyst. In-situ FT-IR experiment was carried over a self-supported pellet of Cu-Na-ZSM-5; the catalyst was dosed with H₂ several times, using the same program used for the reduction mentioned in the experimental. After complete reduction, the catalyst was exposed to a pulse injection of an equimolar mixture of methane and carbon dioxide simultaneously. The in-situ IR spectrum is presented in FIG 6, and showed a peak at 1742 cm⁻¹ which can be attributed to the C=O stretch of acetic acid monomer [35]. An additional peak at 1420 cm⁻¹ confirms the existence of O-H deformation in a dimer of acetic acid, [36] and peaks at 3650 and 2340 cm⁻¹ corresponds to O=C=O stretch of carbon dioxide. The band at 1568 cm⁻¹ is attributed to va(OCO) [37]. Along with the O=C=O, peaks corresponding to strong C-H peaks at 2960, 2922, and 2854 cm⁻¹, as well as peaks corresponding to CO₂ at 2360 and 2340 cm⁻¹ were also observed [22]. This study confirms the formation of acetic acid over reduced Cu-Na-ZSM-5 catalyst.
FIG. 6. In-situ IR spectra for Cu-Na-ZSM-5 at 450°C. The catalyst reduced with hydrogen from room temperature to 450°C then methane and CO₂ introduced simultaneously for 15 min at the same temperature then the IR measured at room temperature.

TEM analysis: More profound evidence on the catalyst deactivation and regeneration, the fresh calcined, used and regenerated catalysts were obtained by TEM as shown in FIG. 7. The TEM micrograph of the synthesized Cu-Na-ZSM-5 and Cu-K-ZSM-5 revealed the formation of the small size of Cu nanoparticles in the range of 1–2 nm and had a good dispersion on ZSM-5. But after the reaction, the TEM image reveals the formation of small Cu aggregates with different size in the range of 4 nm–9 nm. This indicates that the Cu nanoparticles are aggregated resulting in the loss in catalytic activity. The used catalyst was regenerated by calcining in air at 550°C, which shows the re-dispersion of the aggregated Cu particles size into the smaller size of 2 nm–3 nm again. The particle sizes of the catalysts are comparable with the histogram (FIG. S4†).

FIG. 7. HR-TEM images of fresh calcined Cu-Na-ZSM5 (a); Used Cu-Na-ZSM5 (b); Regenerated Cu-Na-ZSM5; fresh calcined Cu-K-ZSM5 (d); Used Cu-K-ZSM5 (e); Regenerated Cu-K-ZSM5 (f).
Proposed mechanism

A plausible mechanism towards the formation of acetic acid through co-activation of CH$_4$ and CO$_2$ on Cu/M$^+$-ZSM-5 zeolite is represented in (SCHEME 1). In the initial step, CH$_4$ activation on Cu/M$^+$-ZSM-5 zeolite creates surface a (-Cu-CH$_3$) species (Step 1). Simultaneously, CO$_2$ activation on M$^+$-ZSM-5 zeolite helps in the formation of surface carbonate species where the basic cations help in surface CO$_2$ adsorption (Steps 1 and 2). These carbonate species acts like a reservoir which in turn promotes insertion into Cu-CH$_3$ bond of copper methyl species (Step 3). These activated surface species transforms into giving a surface acetate intermediate (-Cu-OOCCH$_3$) (Step 4). Which then abstracts a proton from the dissociative cleavage of methane and finally the acetic acid product is desorbed from the surface recovering the active site for the continuation of the catalytic cycle (Step 5). The proton transfer step is the vital step in the acetic acid synthesis. The Cu-exchanged zeolite helps in stabilizing these protons (FIG. S5-S7†).

The simultaneous activation of CH$_4$ and CO$_2$ is of great significance as both contributes towards global warming and can be converted into fuels which are of particular interest in the chemical industry. The C-H activation over transition metals with fcc(111) or hcp(0001) surfaces is reported by Gong et al. where he collected some of the reaction energies calculated previously which hinders methane decomposition [38]. The direct formation of acetic acid in one step with simultaneous activation of methane and carbon dioxide is a thermodynamically unfavorable process and has an atom economy of 100% thus making it important in academic and industrial research. To the best of our knowledge, this is the first report where the continuous formation of acetic acid has been demonstrated experimentally using a unique bifunctional zeolite catalyst. The near-perfect selectivity of acetic acid at equilibrium conditions is attributed to the Cu-exchanged zeolite catalyst which was found to be capable of simultaneous activation of both the reactant species.

SCHEME 1. An ostensible mechanism for the Co-Conversion of CH$_4$ and CO$_2$ into acetic acid over Cu-M$^+$-ZSM-5 Zeolite: (Steps 1 to 3) activation of CH$_4$ leads to the formation of (-Cu-CH$_3$), while the activation of CO$_2$ helps in the
formation of surface carbonate species over cations site. (Steps 4 to 5): insertion of CO\textsubscript{2} into the (-Cu-CH\textsubscript{3}), produces surface acetate species (-Cu-OOCCH\textsubscript{3}) as a reaction intermediate which abstracts the proton to form acetic acid.

**Conclusion**

In summary, we have developed a new direct method for synthesis of acetic acid by co-activation of methane and carbon dioxide in the one-step process. Cu nanoparticle loaded basic cation ZSM-5 catalysts were proven to activate both methane and carbon dioxide simultaneously in concurrent feed, which enabled to the formation of acetic acid in a continuous flow reactor. The activation of CO\textsubscript{2} was observed to be closely related to the alkali cation in the MFI structure. The formation rate of acetic acid was observed to be in the following order with respect to the cationic species K > Na > Ca > Li, this indicates that basic cation contributes to the activated CO\textsubscript{2} on the surface and thus resulted in high insertion activity. The Cu-M\textsuperscript{+}-ZSM-5 catalyst exhibited high starting activity which decreased within an hour but sustained state-state yield on acetic acid of 395 μ mole gcat\textsuperscript{-1} h\textsuperscript{-1} for 10 h. The deactivation was caused mainly due to the aggregation of Cu\textsuperscript{+} species. Upon calcination, the catalyst activity was recovered up to more than 70% which was mainly due to re-dispersion of Cu nanoparticle over the catalyst surface.

**REFERENCES**


