Heterogeneous Catalysis

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NMR-Spectroscopic Evidence of Intermediate-Dependent Pathways for Acetic Acid Formation from Methane and Carbon Monoxide over a ZnZSM-5 Zeolite Catalyst**

Xiumei Wang, Guodong Qi, Jun Xu, Bojie Li, Chao Wang, and Feng Deng**

As a clean energy resource and cheap feedstock, selective conversion of methane into more useful chemicals bears great value in both academic and industrial fields, but remains a tremendous challenge.[1–4] Starting from methane, acetic acid is usually produced by a well-established process that relies on an indirect syngas ($CO+H_2$) route. Since the pioneering work of Sen and Lin[5] and Fujiwara and co-workers[6] who found that acetic acid can be produced directly by carbonylation of methane with CO in a homogenous catalysis system, considerable efforts have been devoted to the direct strategy.[7–11] However, the use of acid as solvent (such as CF_3COOH) and precious metal (Pd and Pt complex) in the carbonylation reaction may conflict with the modern industrial expectations. The carbonylation of isobutane was the first reported example for the conversion of saturated alkanes to produce ketone and carboxylic acid on environmentally friendly heterogeneous solid catalysts.[12] Moreover, promising potential has been demonstrated for the conversion of methane into acetic acid and derivatives over Rh-doped $FePO_4$[13] and sulfated zirconia solid catalysts.[14] However, to our knowledge, carbonylation of methane by CO has rarely been reported over acidic zeolite catalysts that have been widely used in the chemical and petrochemical industry.

There is a general consensus in the carbonylation reaction that the alkyl group of the final oxygenated product originates from the organic reactant whereas the carbonyl group originates from CO. For the carbonylation of methanol with CO over solid catalysts, the classic Koch-type mechanism has been widely accepted, in which the methoxy intermediate formed from methanol reacts with CO to generate an acylium cation, which can be trapped by water to produce carboxylic acid.[15] A similar mechanism for the carbonylation of dimethyl ether was also proposed[16] and confirmed by solid-state NMR spectroscopy on acidic zeolite catalysts.[17] Although such a mechanism is straightforward for the carbonylation of methane in the $FHSO_3$-SbF_5 liquid superacid,[18,19] so far it has not been proved on solid catalysts owing to the lack of experimental evidence for the formation of methoxy species or methyl cation intermediates during the carbonylation process.

Herein, we used in situ solid-state NMR spectroscopy to monitor the carbonylation of methane with CO over ZnZSM-5 zeolite catalysts. We found that acetic acid could be generated directly under mild reaction conditions (573–623 K) through two parallel reaction pathways. Namely, CO is activated into methoxy intermediates, which can further interact with CO to generate acetic acid (Koch-type mechanism), while methane is activated into zinc methyl intermediates that can be consequently transformed into methyl groups of acetic acid with CO_2 through a typical organometallic reaction.

The ZnZSM-5 catalyst was prepared by reaction of metallic Zn vapor with HZSM-5 zeolite in a CAVERN device (Figure S1 in the Supporting Information; CAVERN = cryogenic adsorption vessel enabling rotor nestling).[20] XRD and ^{27}Al magic-angle-spinnig (MAS) NMR spectroscopy results indicated that the Zn modification of HZSM-5 did not lead to observable structural changes of the zeolite framework and the appearance of extra-framework Al (Figures S2 and S3 in the Supporting Information). In situ ^{13}C NMR spectroscopy was employed to monitor the carbonylation reaction (Figure 1). After heating the ZnZSM-5 catalyst co-fed with both ^{13}C-labeled $^{13}CH_4$ and ^{13}CO for one hour at 523 K, in addition to the signal of unreacted methane at $\delta=-7$ ppm (the signal of CO is absent in the CP/MAS NMR spectra), a strong signal appears at $\delta=173$ ppm, which corresponds to surface formate species[21] (Figure 1a). In addition, two other weak signals are observed at $\delta=58$ and -20 ppm, which can be assigned to surface methoxy species[21] and zinc methyl species,[22] respectively. The methoxy species are generally considered as active intermediates in catalytic reactions, such as the conversion of methanol,[17] while the zinc methyl species might possess similar reactivity to organozinc compounds in forming hydrocarbons and/or oxygenated products.[23] The carbonylation reaction begins to occur on the ZnZSM-5 catalyst at 623 K (Figure 1b), which is evidenced by the appearance of methyl ($\delta=21$ ppm) and carbonyl groups ($\delta=187$ ppm) of acetic acid.[14] The decomposition of methoxy species may produce a small amount of ethane ($\delta=6$ ppm).[17] More interestingly, when a trace of molecular oxygen is also added, the amount of zinc methyl

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[*] X. M. Wang, G. D. Qi, Dr. J. Xu, B. J. Li, C. Wang, Prof. Dr. F. Deng
Wuhan Center for Magnetic Resonance, State Key Laboratory
Magnetic Resonance and Atomic Molecular Physics
Wuhan Institute of Physics and Mathematics
Chinese Academy of Sciences
Wuhan 430071 (China)
E-mail: dengf@wipm.ac.cn
xujun@wipm.ac.cn

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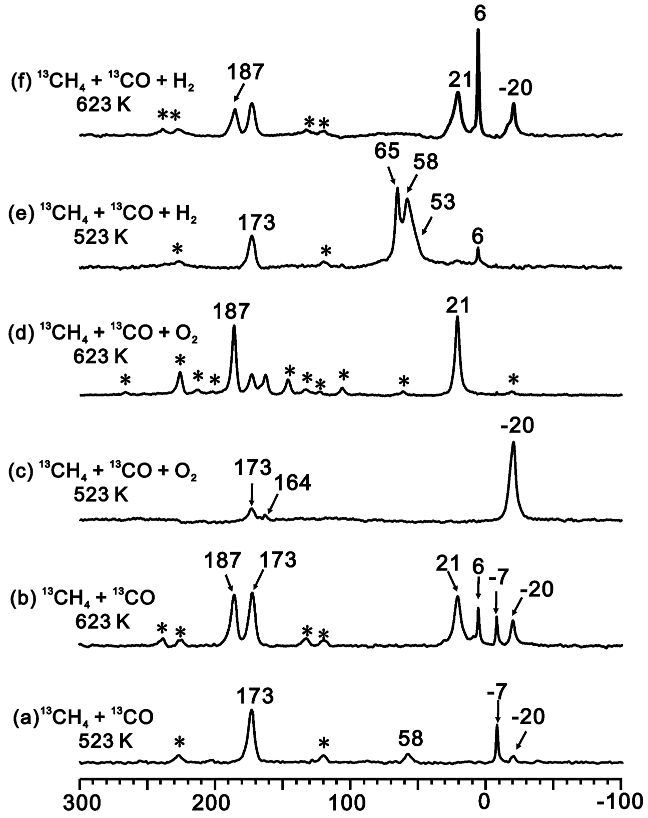


Figure 1. ^{13}C CP/MAS NMR spectra of products formed from co-adsorption of methane and carbon monoxide on ZnZSM-5 catalyst heated for one hour. a, b) $^{13}CH_4$ and ^{13}CO at 523 K and 623 K. c, d) $^{13}CH_4$, ^{13}CO, and O_2 at 523 K and 623 K. e, f) $^{13}CH_4$, ^{13}CO, and H_2 at 523 K and 623 K. Asterisks denote spinning side bands. CP/MAS NMR spectroscopy is cross-polarization magic-angle-spinning NMR spectroscopy.

species ($\delta = -20$ ppm) is significantly increased at 523 K while the methoxy species is unobservable (Figure 1 c). In the meantime, a small amount of formate ($\delta = 173$ ppm) and carbonate species ($\delta = 164$ ppm) is observable as well. Further increasing the reaction temperature to 623 K results in selective formation of acetic acid and complete consumption of methane (Figure 1 d). In contrast, when a trace of H_2 is also adsorbed, the signals of the methoxy species and the derivatives dimethyl ether ($\delta = 65$ ppm) and methanol ($\delta = 53$ ppm) are remarkably increased at 523 K (Figure 1 e). Acetic acid is formed along with the zinc methyl species and ethane (Figure 1 f). To gain insight into the mechanism underlying the carbonylation reaction, ^{13}C-labeled reactants are alternatively employed, because then the origin of the carbon atoms in the observed products can be traced to methane or carbon monoxide, and thus their corresponding role for the formation of acetic acid can be identified (Figure 2).

When ^{13}C-labeled $^{13}CH_4$ and unlabeled CO are used, the zinc methyl species ($\delta = -20$ ppm) is solely produced at 523 K (Figure 2 a), thus confirming that methane can be initially activated though heterolytic dissociation on isolated Zn^{2+} ions in Zn-modified HZSM-5 zeolites.[24–26] Further increasing the reaction temperature to 623 K leads to the appearance of the methyl group ($\delta = 21$ ppm) of acetic acid at the expense of methane, thus unequivocally indicating the intermediate role of zinc methyl species and the contribution of methane to acetic acid (Figure 2 b). By analogy to the reaction of organozinc compounds,[23] the zinc methyl species could be directly trapped by CO_2 to give the methyl and carbonyl groups of acetic acid, respectively (pathway 1 in Scheme 1). Generally, CH_3COO^- transient species were proposed as intermediates for the reaction of CH_4 and CO_2 in the liquid acid system.[27] Since no carbonyl groups are observed in Figure 2 b, the methyl group of acetic acid is solely generated from methane, whereas the unobservable carbonyl group should originate from CO_2 that is formed in situ by oxidation of ^{13}C-unlabeled CO. The formation of CO_2 is supported by the ^{13}C MAS NMR spectrum when ^{13}C-labeled ^{13}CO is used (Figure S4 in the Supporting Information).

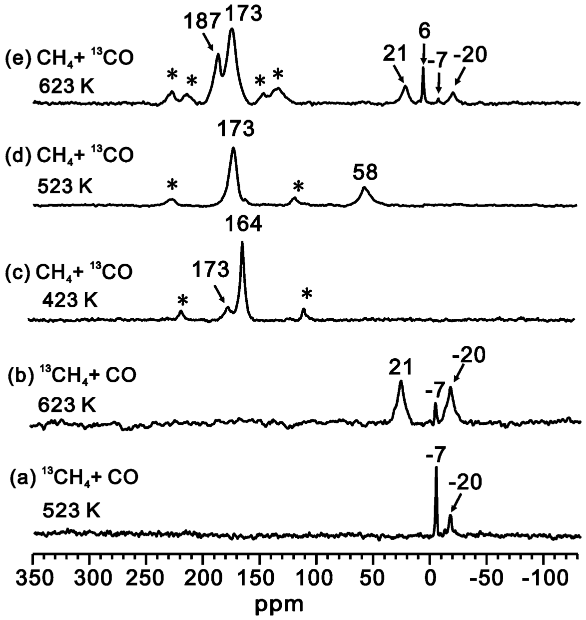
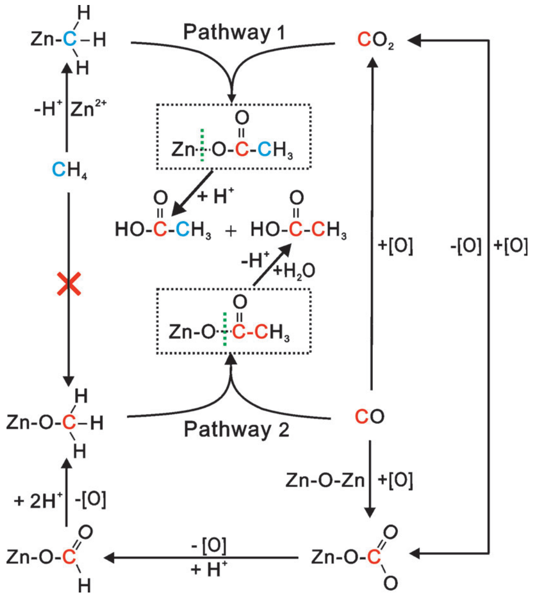


Figure 2. ^{13}C CP/MAS NMR spectra of products formed from co-adsorption of methane and carbon monoxide on ZnZSM-5 heated for one hour. a, b) $^{13}CH_4$ and CO at 523 K and 623 K. c, d, e) CH_4 and ^{13}CO at 423 K, 523 K, and 623 K. Asterisks denote spinning side bands.

When ^{13}C-unlabeled CH_4 and labeled ^{13}CO are used, both formate ($\delta = 173$ ppm) and carbonate species ($\delta = 164$ ppm) are formed at 423 K (Figure 2 c). With the reaction temperature going up to 523 K, the formate signal grows at the expense of the carbonate signal, and the signal of the methoxy species appears at $\delta = 58$ ppm (Figure 2 d). Thus, the observed carbonate, formate, and methoxy species are expected to have originated from carbon monoxide. In this case, carbon monoxide is firstly oxidized into carbonate species, then transformed into formate species through hydrogenation at elevated temperature, and further hydrogenated into methoxy species (pathway 2 in Scheme 1). It was reported that CO and CO_2 could be converted into carbonate and formate species over ZnO containing oxide catalysts.[28–30] Here, Zn−O−Zn clusters may probably be the oxidation centers (Figure S2 in the Supporting Information), and



Scheme 1. Proposed reaction pathways for the formation of acetic acid from methane and carbon monoxide on ZnZSM-5 catalyst. Zn^{2+} stands for isolated Zn^{2+} ions in the ZnZSM-5 catalyst, Zn—O—Zn clusters are the probable oxidation centers, and H^+ are protons from either the bridging hydroxy groups of the ZnZSM-5 catalyst or from the heterolytic dissociation of methane. The two-headed arrow on the right indicates that CO_2 can be converted into carbonate species in the presence of the catalyst, and that in the presence of O_2 the decomposition of carbonates into CO_2 is favored.

protons from either the bridging hydroxy groups (Brönsted acid sites) of the ZnZSM-5 catalyst (Figure S5 in the Supporting Information) or the heterolytic dissociation of methane may be involved in the consecutive hydrogenation process. Further increasing the temperature to 623 K leads to the appearance of both methyl ($\delta = 21$ ppm) and carbonyl ($\delta = 187$ ppm) groups of acetic acid in addition to ethane ($\delta = 6$ ppm) and methane ($\delta = -7$ ppm) from the decomposition of methoxy species,[17] and zinc methyl ($\delta = -20$ ppm) species from the dissociation of methane (Figure 2e).

The experimental result allows us to ascertain that both methyl and carbonyl carbon atoms derive from ^{13}CO in this case. For the methoxy species, the above experiment with labeled ^{13}CO demonstrates its intermediate role during the carbonylation reaction, and that the acetic acid could be formed through the Koch-type mechanism (pathway 2 in Scheme 1). In this mechanism, the acylium cation was generally considered as the precursor of acetic acid, however, it is too active to be observable on zeolite-based catalysts[17] and only stabilized in superacid systems in the absence of water.[19] Actually, when a trace of water is added into the reaction system, the amount of the formed acetic acid is notably increased (Figure S6 in the Supporting Information). This suggests that water can accelerate the reaction by readily trapping the transient acylium cation to generate acetic acid. In our system, the formation of water at 623 K is confirmed by in situ ^1H NMR spectroscopy experiments (Figure S7 in the Supporting Information). At the high reaction temperature, protons from either the Brönsted acid sites or from the heterolytic dissociation of methane can react with formate species to form HCOOH. Decomposition of HCOOH produces H_2 and CO_2,[31] which in turn generates water molecules through the reverse water gas shift reaction that usually occurs in the process of methanol synthesis from CO/CO_2/H_2.[32]

Although two reaction pathways proceed in parallel on the ZnZSM-5 catalyst, one of them can be preferred, depending on which reaction intermediate is predominant. The presence of O_2 favors the formation of zinc methyl species and disfavors the formation of methoxy species owing to facile decomposition of carbonates into CO_2, and thus the hydrogenation process is significantly hindered. In this case, the carbonylation reaction proceeds mainly through pathway 1. On the other hand, adding a trace of H_2 favors the formation of methoxy intermediate by enhancing the hydrogenation of carbonates and formates, which facilitates the carbonylation reaction mainly through pathway 2. In fact, the formation of CO_2 is hindered in this case (Figure S8 in the Supporting Information), and thus the conversion of methane through pathway 1 dramatically decreases.

In summary, the present in situ solid-state NMR spectroscopy studies demonstrate for the first time that methane can be directly carbonylated into acetic acid with CO over the ZnZSM-5 catalyst under mild conditions. Two parallel pathways proceed in a competitive way for the formation of acetic acid. The methoxy intermediate is generated by CO through oxidation and hydrogenation. This species is attacked by residual CO, forming acetic acid through a Koch-type mechanism. On the other hand, methane simultaneously produces a zinc methyl intermediate, which is trapped by CO_2 to form acetic acid. Importantly, the two reaction pathways are likely controllable by varying the redox conditions. The present findings may provide a new perspective for selective conversion of small alkanes and co-reactants into more valuable chemicals on Zn-modified zeolite catalysts.

Experimental Section

The ZnZSM-5 catalyst was prepared by reaction of metallic Zn vapor with HZSM-5 zeolite. In brief, on a vacuum line, HZSM-5 zeolite (Si/Al = 21, NanKai University) was dehydrated at a temperature of 673 K and a pressure below 10^{-3} Pa over a period of 12 h, and Zn powder (99.999%, Sinopharm Chemical Reagent Co, Ltd.) was degassed at a pressure below 10^{-3} Pa at room temperature. Then the dehydrated HZSM-5 and the degassed Zn powder were mixed (with a molar ratio of $Zn/Al > 1$) and transferred into a CAVERN device[20] in a dry nitrogen atmosphere in a glovebox. The CAVERN device was then connected to the vacuum line, and the mixture was heated at a temperature of 773 K and a pressure of 10^{-2} Pa for two hours. The excess of metallic Zn and the released hydrogen were removed by evacuation at the same temperature for another 30 min. The Zn content was approximately 3.8% as determined by inductively coupled plasma analysis.

$^{13}CH_4$ (^{13}C, 99%, Cambridge Isotope Laboratories, Inc.) and ^{13}CO (^{13}C, 99%, Cambridge Isotope Laboratories, Inc.) were introduced onto the activated ZnZSM-5 catalyst in a glass ampule under vacuum at the temperature of liquid N_2, and then the glass ampule was sealed off from the vacuum system. The reaction was performed in the sealed ampule under successively elevated temperatures for a specific reaction period, quenched by liquid N_2, and then the ampule was transferred into a 7.5 mm rotor for NMR spectroscopy measurements.

All solid-state NMR spectroscopy experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer, equipped with a Chemagnetic triple-resonance 7.5 mm probe, with resonance frequencies of 400.13 and 100.6 MHz for ^{1}H and ^{13}C, respectively. Single-pulse ^{13}C MAS experiments with ^{1}H decoupling were performed by using a $\pi/2$ pulse width of 4.8 µs and a repetition time of 10 s. ^{1}H MAS experiments were carried out with a $\pi/2$ pulse width of 5.3 µs and a repetition time of 4 s. The magic angle spinning rate was set to 3–5 kHz. For the $^{1}\mathrm{H}\rightarrow^{13}\mathrm{C}$ CP/MAS NMR experiments, the Hartmann-Hahn condition was achieved using hexamethylbenzene (HMB), with a contact time of 2.0 ms and a repetition time of 2.0 s. The chemical shifts of ^{13}C and ^{1}H were referenced to adamantane.

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