Formation of HCO$^+$ ion by protonation of carbon monoxide in zeolites: the origin of catalytic activity in methanol carbonylation

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Abstract: We show that CO can be protonated by Brønsted acid sites to form the super-electrophilic HCO$^+$ cation in H-zeolites such as mordenite. This reactivity stems from the confining environment of small 8-ring side pockets of H-MOR. HCO$^+$ is a catalytically active super-electrophile: it carbonylates dimethyl ether and hydrocarbons to methyl acetate and aldehydes.
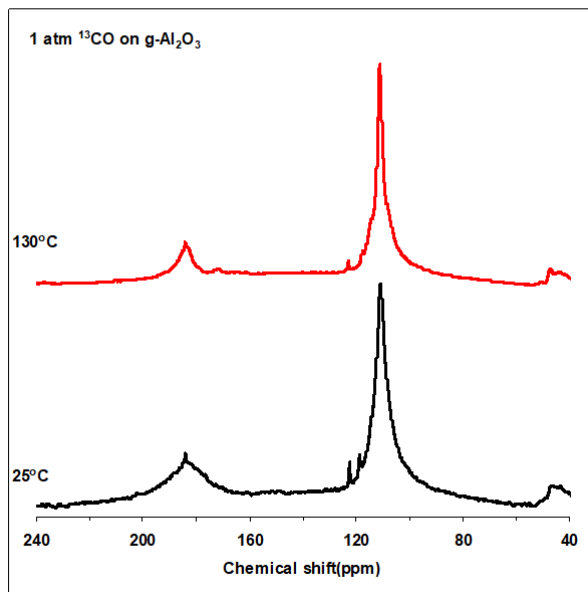
Zeolites are industrially important crystalline and microporous materials composed of tetrahedral SiO$_4$ and AlO$_4$ units [1]. They are used industrially as adsorbents and catalysts for cracking, reforming, methanol to olefin (MTO) and other reactions [1-5]. Despite intense research, various catalytic processes that occur on zeolites took decades to understand mechanistically. Methanol to olefin process, for example, is thought to occur through hydrocarbon pool mechanism with alkylated aromatics being the catalytically important intermediates [6]. The origin of cracking activity of steamed/dealuminated zeolites has been discussed for over six decades and attributed to enhanced Bronsted acidity of steamed zeolites [2]. Very recently, we revealed that increased cracking catalytic activity stems from the presence of Al$_2$O$_3$ clusters in the steamed/dealuminated zeolite with penta Al$_1$O$_5$ sites that break the first alkane C-H bonds very effectively with the following steps occurring on Bronsted acid sites [7].

Among recent developments of zeolites catalytic chemistry, methanol carbonylation activity to form acetic acid from (CH$_3$OH + CO) or methyl acetate from (dimethyl ether + CO) that was first described on H-Zeolite catalysts by Fujimoto [8] has recently gained a lot of attention. Experimental efforts [8-11] identified that zeolites containing 8-membered rings, such as H-MOR, FER, SSZ-13 and SSZ-39 possess good activity for this catalytic process whereas large-pore

zeolite such as H-FAU, for example, do not show high activity. Theoretical studies on solid catalysts suggested that the reaction occurs through the formation of methyl cation (CH_3^+) in zeolite via methanol protonation on Bronsted acid sites [8-11]. This cation, however, has never been detected. In fact, no direct or indirect evidence exists for the formation of carbenium ions in zeolites with C number lower than C4. On the other hand, solid-related methanol carbonylation studies have not discussed the possibility of CO protonation in zeolites to form HCO^+. HCO^+ and HN_2^+ ions are one of the most important molecules in the space chemistry, and, although encountered in extremely small amounts, they are the primary molecular ions found in molecular clouds [12-14]. HN_2^+ has never been identified in the condensed phase until we recently showed its existence in small-pore H-SSZ-13 zeolite as an intermediate during environmentally important catalytic reduction of NO^+ ion to N_2 with NH_3 [15] at low temperatures (thus, establishing the hitherto unrecognized role of NO^+ and HN_2^+ in selective catalytic reduction of NO with ammonia). HCO^+ search has been conducted in superacids [16,17] for many decades to no avail, until recently Gladysz and Horvath finally caught this fleeting cation in super-acids at very high pressures ~30-85 atmospheres using in-situ NMR studies [16].

We now detect its formation in zeolites under mild conditions. We used solid-state NMR spectroscopy with ^{13}C labeled CO: putting CO in zeolites HY (large pores) and, for example, solid acid [12] gamma-alumina does not lead to the formation of HCO^+ (Fig. 1).
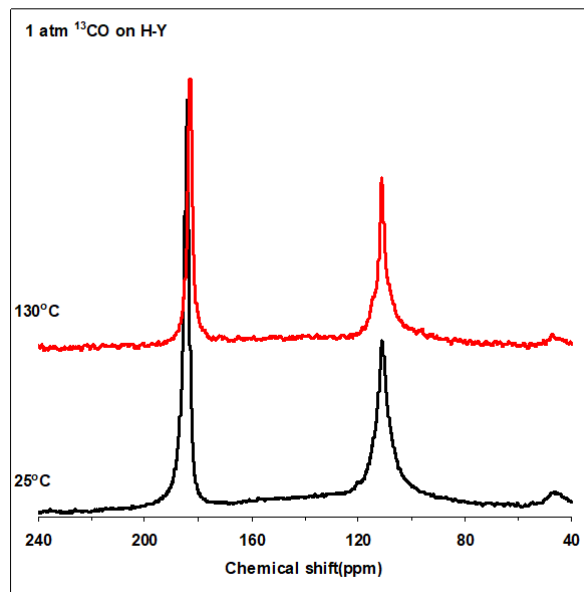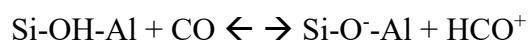
Fig. 1. ^{13}C NMR in the presence of 1 atm CO on gamma-alumina and H-Y with Si/Al ~ 2.5 at 25 and 130 ºC, respectively. No evidence for HCO$^+$ cation formation can be found.
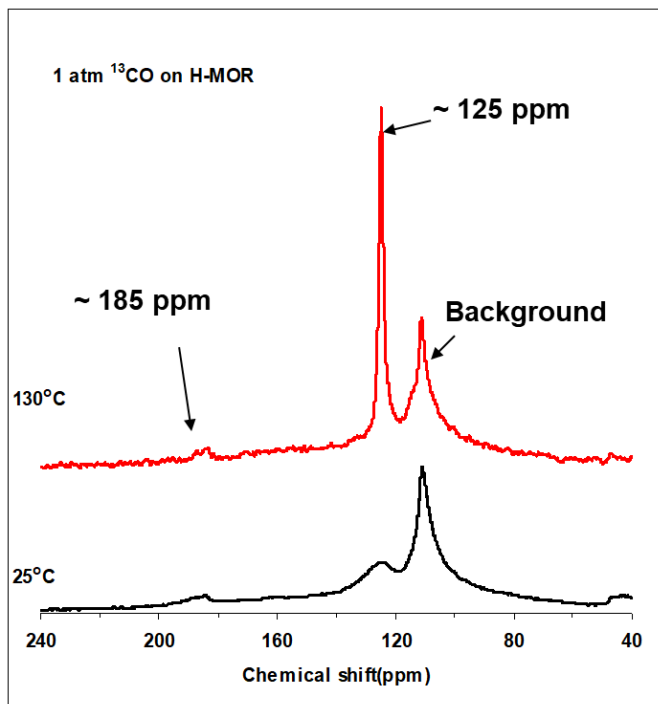
When we reacted H-MOR with Si/Al ratio ~ 6.5 with [13]CO at 1 atmosphere, at 25 ºC, we saw the evolution of a typical signal for physisorbed CO at ~ 185 ppm. At room temperature, no new features appeared except this signal. As we increased the temperature to 130 ºC, however, the new signal appeared at ~125 ppm. The only chemistry possible at elevated temperatures in zeolites is the ability of Bronsted acid protons of Si-OH-Al groups of zeolite to "move" and protonate molecules (see further discussion in the text and reference [18]). In the presence of 1 bar gas-phase CO, the chemistry that can occur is protonation of carbon monoxide with H$^+$:

Si-OH-Al + CO $\longleftrightarrow$ Si-O$^-$-Al + HCO$^+$

Thus, we assign the feature at ~125 ppm to HCO$^+$ cation in zeolitic micropores (Fig. 2, top graph) which is in agreement with approximate theoretical value of formyl cation in the gas phase ~135 ppm [16].

In the presence of methanol, HCO$^+$ reacts with dimethyl ether forming methyl acetate product, as evidenced by ^{13}C NMR studies (Fig. 2, bottom graph). On HY or alumina, HCO$^+$ signal is not formed in any observable amounts consistent with no/very little reactivity is observed for methanol carbonylation, further corroborating our conclusion that the presence of HCO$^+$ is indispensable for the formation of methyl acetate. The difference between HY and MOR is that MOR has side pockets with 8-membered rings. Actually, all zeolites that possess high DME carbonylation activity have 8-membered rings in their structure [8]. Clearly, confinement of HCO$^+$ in those rings is extremely important and provides optimal fit for us to observe this reactivity. Other zeolites still have some activity, but too large (10-MR and higher) or too small pores (6-MR and lower) lead to very small methyl acetate yields. Furthermore, temperatures when HCO$^+$ is observed are the temperatures when Bronsted acid ions begin the process known as "hopping" – under normal conditions, they are not detached from the framework, but as the temperature goes up they begin to "hop" between different Si-OH-Al sites [18], therefore detaching from the framework. Gas-phase CO catches this detached proton and forms the HCO$^+$ ion. The HCO$^+$ ion in zeolite is super-electrophilic [17,19]: it shows activity for dimethyl ether carbonylation as well as alkane carbonylation. Activation of strong bonds by this *non-metal* super-elecrophile shows similarities to how super-electrophilic *metal* cations, described by us very recently in zeolites [19,20], activate

strong C-H bonds: HCO$^+$ is so "hungry" for electron density that it is capable of inserting itself in the very strong C-H bond of alkane, forming Alkyl-C(=O)H aldehyde, for example. We further preformed *in-situ* infra-red studies on H-MOR sample. Notably, we observed HCO$^+$ ion C-O stretch at ~2207 cm^{-1} (Fig. 3) (gas-phase HCO+ is 2184 cm^{-1} [14]).
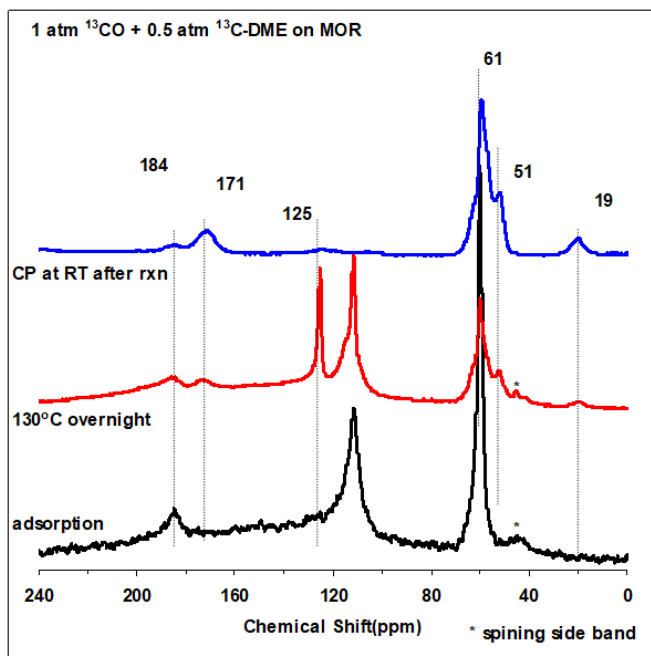
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Fig. 2. Top graph: ^{13}C NMR in the presence of 1 atm CO on H-MOR with Si/Al ~ 6 at 25 and 130 ⁰C, respectively. The ~185 ppm belongs to physisorbed CO. The band at 125 ppm belongs to HCO$^+$ cation. Bottom graph: monitoring of ^{13}C dimethyl ether (0.5 atm) and ^{13}CO (1 atm) at room temperature, at 130 ⁰C and cross-polarization NMR spectrum after cooling down to room temperature. It is evident that methylacetate is formed with the characteristic ^{13}C bands at 20, 51, 171 ppm. DME ^{13}C band is at 61 ppm.
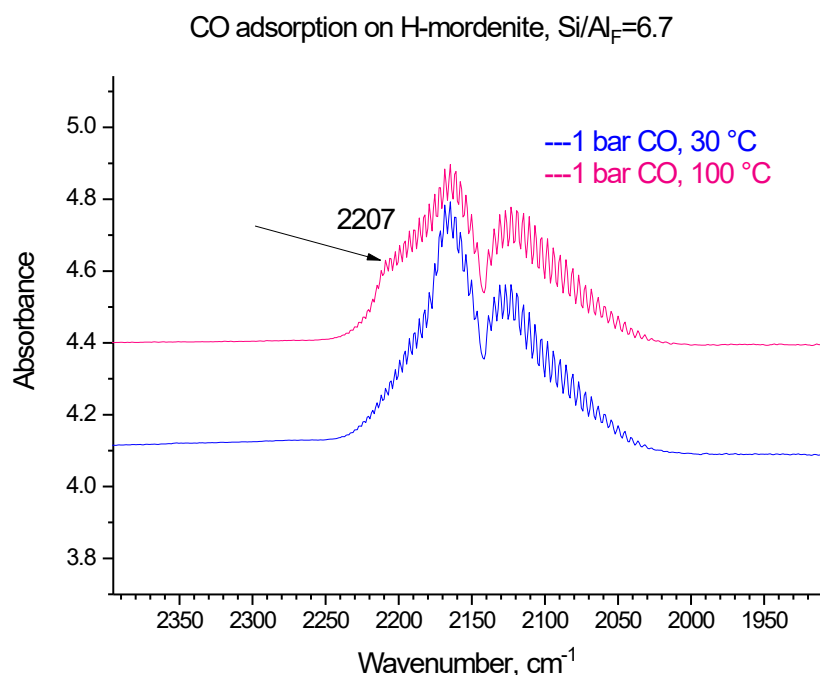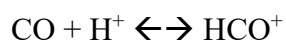
CO adsorption on H-mordenite, Si/Al$_F$=6.7

Fig. 3. FTIR of C-O stretching region under 1 bar CO pressure for H-MOR with Si/Al ~ 6.5 (pre-treated at 500 ⁰C before measurement) at 30 ⁰C (blue line) and 100 ⁰C (red line).

In summary, we show unprecedented formation of super-electrophilic HCO$^+$ ions in zeolite H-MOR under mild conditions. We suggest it is the catalytically active intermediate for methanol carbonylation (and not CH$_3^+$ ions as suggested in all previous studies on solid catalysts [8-11]). The carbonylation catalytic scheme can be written as such (Scheme 1):

$$CO + H^+ \longleftrightarrow HCO^+$$
$$HCO^+ + CH_3\text{-}O\text{-}CH_3 \rightarrow [CH_3\text{-}C^+(\text{-}OH)\text{-}OCH_3] \rightarrow CH_3\text{-}C(=O)\text{-}OCH_3 + H^+$$

HCO$^+$ can be observed with ^{13}C NMR studies presumably due to favorable energetics (confinement) in 8-membered-ring side-pockets of H-MOR. Remarkably, the activity of this non-metal containing ion resembles activity of super-electrophilic transition metal cations, recently proven to exist in zeolites [19]. Our study opens up a new chapter of CO chemistry on solid materials and provides new insight into catalytic mechanism of zeolites for important organics transformations.

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Materials and methods

MOR zeolite is the Na form with Si/Al ratio ~ 6.5 was obtained from Zeolyst. The sample was exchanged with 0.5 M ammonium nitrate solution three times at 80 ^{o}C, the resulting powder washed and dried first at 100 ^{o}C, then at 550 ^{o}C in the dry air flow. The resulting powder was kept in the glove box in the absence of moisture.

Na-FAU (Na-Y) with Si/Al ~ 2.5 was supplied by Zeolyst. The sample was exchanged with 0.5 M ammonium nitrate solution two times at 80 ^{o}C, the resulting powder washed and dried first at 100 ^{o}C, then calcined at 550 ^{o}C in the dry air flow. The resulting powder was kept in the glove box in the absence of moisture.

Gamma-alumina (SBA-200, SASOL, high-purity) was calcined at 600 ^{o}C and stored in the glove box prior to measurement.

The *in-situ* static transmission IR experiments were conducted in a home-built cell housed in the sample compartment of a Bruker Vertex 80 spectrometer, equipped with an MCT detector and operated at 4 cm^{-1} resolution. The powder sample was pressed onto a tungsten mesh which, in turn, was mounted onto a copper heating assembly attached to a ceramic feedthrough. The sample could be resistively heated, and the sample temperature was monitored by a thermocouple spot welded onto the top center of the W grid. The cold finger on the glass bulb containing CO (99.995%) was cooled with liquid nitrogen to eliminate any contamination originating from metal carbonyls.

^{13}C and ^{13}C CP measurements were conducted on a Varian Inova 300 MHz spectrometer. The corresponding ^{13}C Larmor frequency was 75.43 MHz. Spectra were externally referenced to adamantane at 38.48 ppm and a sample spinning rate of 3.4 kHz at the magic angle was employed. Air-tight NMR cell was used to expose the powder sample (loaded in the NMR rotor in the glovebox) to the desired amounts of ^{13}CO (Sigma aldrich, 99%) and ^{13}C dimethyl ether (Cambridge Isotopes, 99%). The rotor could then be transferred to NMR without exposure to ambient atmosphere.

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