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Direct observation of DME carbonylation in the different channels of H-MOR zeolite by continuous-flow solid-state NMR spectroscopy†

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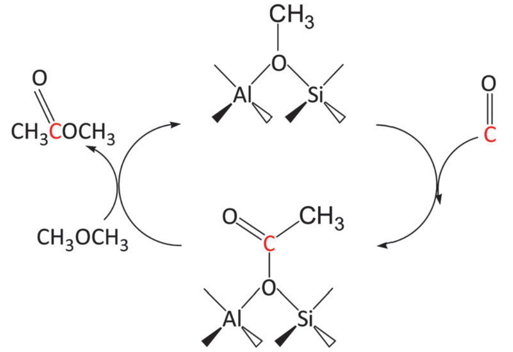
The dynamic evolution of acetyl intermediates in the two different channels of H-mordenite (H-MOR) zeolite during dimethyl ether (DME) carbonylation is tracked by using *in situ* solid-state NMR spectroscopy under continuous-flow conditions. Thus, the reaction path *via* methyl acetate produced over active sites in 8 member ring (MR) channels, followed by diffusion into 12 MR channels, is proposed.

Carbonylation of methanol or ether with CO is the main approach to synthesize acetic acid and esters, which are widely used in the chemical industry.[1] However, the processes based on Rh or Ir complex catalysts with halide promoters are costly and environmental unfriendly. In 2006, Iglesia and co-workers reported the production of methyl acetate (MA) using H-MOR zeolites, yielding a selectivity more than 99%, *via* carbonylation of DME with CO at 423–463 K.[2] It was also suggested that the reaction of CO decomposed from methanol with methyl groups to acetyl groups might be another intrinsic mechanism for C–C bond initialization in the MTO reaction.[3,4] The following mechanism had been proposed: DME interacted with Brønsted acid sites on zeolites to generate methoxyl, and then CO was inserted into methoxyl to form an acetyl intermediate which reacted quickly with another dimethyl ether to produce MA and form a methoxyl on Brønsted acid sites (Scheme 1).[5,6] Based on density functional theory (DFT) calculations, Corma *et al.* concluded that methanol carbonylation preferentially occurred in 8 member ring (MR) channels, while hydrocarbon formation occurred in 12 MR channels.[7,8] However, direct experimental evidence for the proposed mechanism is still lacking to date.

In situ solid state NMR spectroscopy, as an efficient technique to directly observe the surface species on catalysts, has been applied to investigate many reactions with solid acid catalysts.[9–13] Hunger *et al.* first used the continuous-flow solid state NMR technique to study the methanol reaction on HY zeolites. They investigated methoxyl and its derivates, and the related reactions on Y zeolite using *in situ* solid state NMR spectroscopy.[14] Stepanov *et al.* concluded that the acetate group is bound to the Keggin anion on $Rh/Cs_2HPW_{12}O_{40}$ by using the *in situ* NMR method.[11] Indeed, Blasco *et al.* had confirmed the acetyl species (CH_3CO–) rather than the acylium cation ($CH_3(CO)^+$) as a stable surface species during methanol carbonylation on zeolites, which is represented by a completely different signal (170 ppm).[15] But Deng *et al.* observed the acetyl species on MOR zeolite by its characteristic chemical shift anisotropy (CSA) parameters, because it has the same chemical shift (185 ppm) as that of the carbonyl group of MA.[16] It is a controversial issue concerning the existence of acetyl species. Furthermore, the above studies were conducted in sealed glass ampoules under batch-like conditions. However, the investigation of the intermediates of heterogeneous reactions, especially for the unstable species, requires continuous-flow reaction conditions. Here, we present direct experimental evidence for the acetyl intermediate involved in DME carbonylation on H-MOR zeolite using *in situ* continuous-flow ^{13}C MAS NMR spectroscopy. The deconvolution of the spectroscopic data of the adsorbed species on zeolites was further supported by DFT results.



Scheme 1 Mechanism of DME carbonylation with CO on H-MOR.

Fig. 1 shows the *in situ* ^{13}C MAS NMR spectra of H-MOR zeolite recorded during the carbonylation of DME at 453 K.

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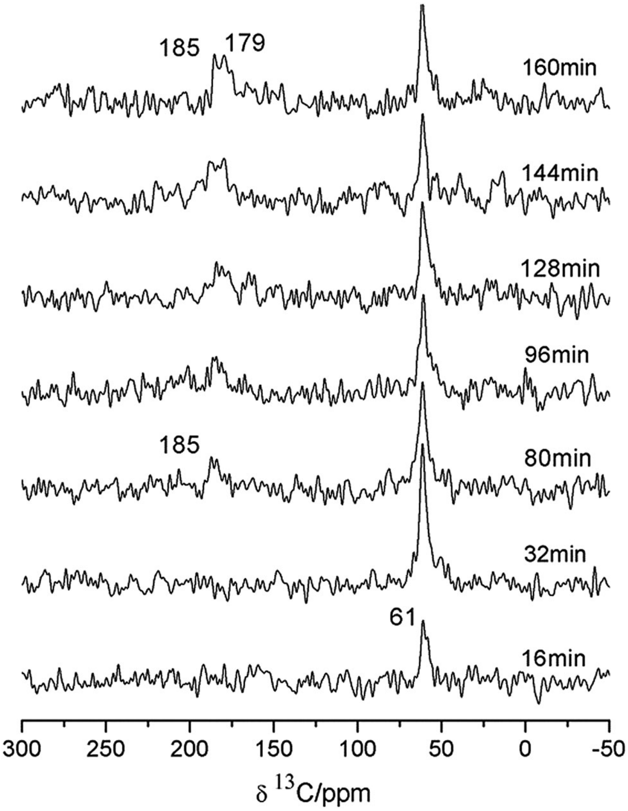

Fig. 1 *In situ* ^{13}C MAS NMR spectra of H-MOR zeolite recorded during the conversion of DME at 453 K. Each spectrum was accumulated by 500 scans at a spinning rate of 3 kHz.

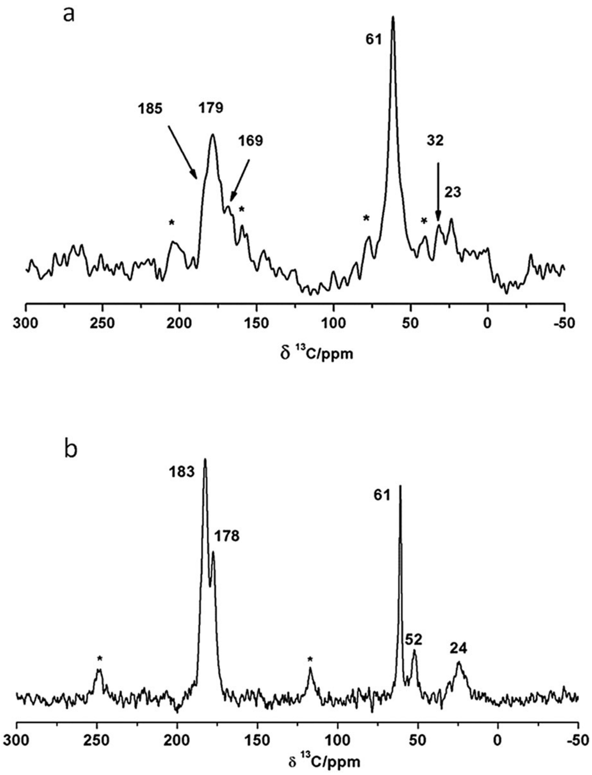

Fig. 2 *In situ* continuous-flow ^{13}C MAS NMR spectra (a) after exposure to a gas mixture (5% DME (natural abundance), 50% CO (50% ^{13}C labelling), 45% He) for 160 min at 453 K; it is accumulated by 2000 scans and at a spinning rate of 3 kHz. The asterisks denote spinning sidebands. (b) ^{13}C CP MAS NMR spectra of the sample after the *in situ* reaction.

H-MOR (Si/Al = 10) was obtained by ion exchange from Na-mordenite described elsewhere.[17,18] After transferring the sample into a 7 mm Bruker MAS-CAT NMR probe, it was pre-treated at 673 K for 30 min under flowing He (60 mL min^{-1}) for dehydration. Then, the gas mixture (5% DME (natural abundance), 50% CO (50% ^{13}C labelling), 45% He) was injected into the MAS NMR rotor reactor at 453 K, and the ^{13}C MAS NMR spectra were recorded. For the first 16 min, the highly overlapped ^{13}C resonance peaks from 40 to 65 ppm appear. This feature can be deconvoluted into three characteristic resonance peaks, which could be assigned to the surface species of DME adsorbed on H-MOR (δ = 61 ppm), methanol adsorbed on Brønsted acid sites (δ = 52 ppm), and the methoxyl produced by DME interacted with Brønsted acid sites (δ = 58 ppm). In order to distinguish these three species, further experiments have been performed under *ex situ* conditions, and the details are shown in the ESI† (Fig. S1). After 80 min, the carbonyl ^{13}C resonance peaks at 160–190 ppm arose gradually, indicating that abundant methoxyl acetate began to accumulate on the catalyst after the induction period. It was clear that DME adsorption onto the zeolite and formation of methoxyl occurred on Brønsted acid sites, which agrees with the measurements from mass spectroscopy (MS) (see the ESI,† Fig. S2). The signals from carbonyl groups increased gradually, but the signal to noise ratio was too low to be identified.

Fig. 2a shows the *in situ* continuous-flow ^{13}C MAS NMR spectrum after the gas mixture has been injected into the reactor at 453 K for 160 min. The spectrum was accumulated by 2000 scans and the signal to noise ratio was improved. The signal at 61 ppm with a shoulder at 63 ppm is observed at the beginning of reactions, which were previously attributed to the DME adsorbed on Brønsted acid sites in end-on and side-on conformations.[14] The methoxyl groups on H-MOR zeolite have a chemical shift of 58 ppm (see ESI,† Fig. S1), which is in agreement with Bosacek's work.[19] The signals at 185 and 179 ppm should be assigned to the carbonyl groups of MA adsorbed in 8 MR channels and 12 MR channels, respectively.[16] The confined environment of zeolites makes the signal from the 8 MR channels move to low field. The δ = 179 ppm signal from the 12 MR channels is close to that from MA in liquid (δ = 177 ppm). The CP (cross polarization) technique can increase the sensitivity of ^{13}C nuclei by cross-polarization from ^{1}H to ^{12}C. After *in situ* continuous-flow experiments, the ^{13}C CP MAS NMR spectrum (Fig. 2b) recorded at room temperature with a spinning rate of 12 kHz indicates that the two carbonyl signals are definitely distinguished from each other. The signal at 23 ppm should be attributed to the methyl group of MA. The signal at 169 ppm shown in Fig. 2a should also be assigned to the carbonyl group, but it wasn't observed in Fig. 2b. We speculate that this signal may come from an active species that can only survive under *in situ* conditions.

We calculated the chemical shifts of all species involved in this reaction on H-MOR by DFT. Table 1 summarized the calculated and

Table 1 ^{13}C chemical shifts of surface species adsorbed on the H-MOR zeolites obtained by DFT calculations and experiments

Species		δ ^{13}C calculated by DFT (ppm)	δ ^{13}C from experiments (ppm)
Methoxyl	Methoxyl	62.6	58.4
Acetyl	Carbonyl	169.2	169
	Methyl	26.1	34
MA in 12 MR	Carbonyl	181.7	179
	Methoxyl	55.3	54
	Methyl	22.7	24
MA in 8 MR	Carbonyl	188.4	185
	Methoxyl	60.3	54
	Methyl	26.1	24
DME	Methoxyl	63.5	63
Methanol	Methoxyl	—	52

experimental ^{13}C NMR isotropic chemical shifts of the methyl and carbonyl groups of methoxyl acetate adsorbed onto the Brønsted acid sites of the zeolite (see details of DFT calculation in the ESI†). The calculated ^{13}C NMR chemical shifts for the surface acetyl species are well consistent with the experimental results.

The signal at 169 ppm can be ascribed to the surface acetyl species (CH_3CO-Z Z for zeolites),[15] which is consistent with the theoretical calculations. The signal at 32 ppm might be attributed to the methyl group of the surface acetyl species. As an unstable intermediate, acetyl species can be subsequently captured by water to produce acetic acid, by methanol or dimethyl ether to give MA, or by ammonia to yield acetamide as reported by earlier research studies. The acetyl species bound to an oxygen atom of the catalyst has been reported to be the intermediate in the carbonylation of methanol on the 12-tungstophosphoric acid catalyst (12-$H_3PW_{12}O_{40}$), based on the appearance of ^{13}C MAS NMR signals at δ $^{13}C(CO)$ = 193 ppm and δ $^{13}C(H_3C–)$ = 22 ppm attributed to the CH_3–CO–(O–W) species.[20] We did not observe the surface acetyl species by the *ex situ* experiments (Fig. 3), because it is quite unstable at room temperature.

An additional *ex situ* continuous-flow experiment was carried out in order to distinguish the signals at 179 and 185 ppm. The dehydrated H-MOR zeolite was treated at 453 K with a continuous-flowing gas mixture (50% CO, 5% DME, 45% He, 30 ml min^{-1}) in the reactor. After the induction period, it was switched to another gas mixture (50% ^{13}CO, 5% DME, 45% He, 30 ml min^{-1}). After 5 and 10 min respectively, the gas flow was stopped, and liquid N_2 was injected subsequently to cool the catalyst. The obtained sample was then transferred into an NMR rotor in a glove box. The corresponding ^{13}C CP MAS NMR spectra are shown in Fig. 3a and b. It is found that the carbonyl peak of MA in 8 MR channels at δ 185 ppm appeared earlier than the carbonyl signal from the 12 MR channels at δ 179 ppm. The results indicate that carbonylation takes places in 8 MR, and then the MA diffuses into 12 MR. These results demonstrate that the surface acetyl species cannot be observed in *ex situ* continuous-flow experiments, whereas the continuous-flow *in situ* ^{13}C MAS NMR spectroscopy enables direct observation of the intermediates.

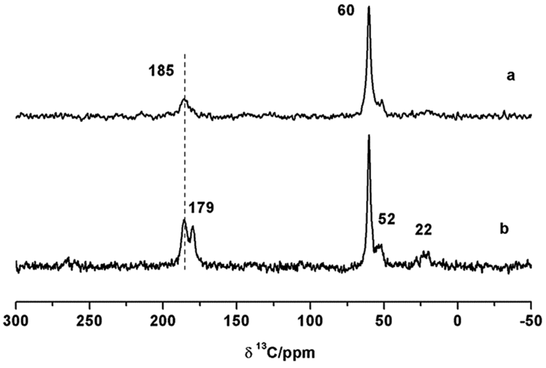

Fig. 3 *Ex situ* continuous-flow ^{13}C CP MAS NMR spectra after the gas mixture has been injected into the reactor at 453 K for (a) 5 minutes and (b) 10 minutes, respectively, recorded at room temperature and at a spinning rate of 12 kHz.

Overall, the surface acetyl intermediates on H-MOR zeolites (CH_3CO-Z) were detected during DME carbonylation using *in situ* continuous-flow ^{13}C MAS NMR spectroscopy. The *ex situ* experiments show that the carbonyl peak of MA in the 8 MR channels appeared prior to the carbonyl signal from the 12 MR channels, indicating that the carbonylation reaction likely takes place within the narrow 8 MR channels while the broader 12 MR channels provide a channel for the transport of reactants and products. This explains the much better activity and selectivity of carbonylation on H-MOR than on other zeolite containing 8 MR channels. These results also imply that the carbonylation of methylated zeolites could initiate the formation of a hydrocarbon pool in the MTO reaction.

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