# Kinetic studies of the dehydration of methanol over aluminosilicate and gallosilicate offretites

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The kinetics of the dehydration of  $CH_3OH$  by the hydrogen forms of three offretites with different contents of framework Al and Ga have been monitored by <sup>13</sup>C magic-angle-spinning (MAS) NMR spectroscopy. No reaction takes place at room temperature. At 150 °C methanol is dehydrated to dimethyl ether. As expected, the catalytic activity of offretite for this reaction is lower than that of zeolite ZSM-5, and it decreases with increasing framework gallium content. The rates of the dehydration reaction are 0.045, 0.863 and 1.136 a.u.<sup>-1</sup> s<sup>-1</sup> for Ga-, Al,Ga- and Al-offretites, respectively.

Microporous molecular sieves, such as zeolites and AlPO<sub>4</sub>based materials, are Brønsted acids and can selectively accommodate a variety of small molecules, which makes them powerful shape-selective catalysts.<sup>1</sup> Among the multitude of chemical reactions catalysed by these materials, one of the most important industrially is the methanol-to-gasoline (MTG) process in which methanol (MeOH) is first dehydrated to dimethyl ether (DME), which is then converted to gasoline, a mixture of  $C_5$ - $C_{10}$  hydrocarbons.<sup>2,3</sup> There has been much interest in the nature of the intermediate species involved, but the mechanism of the various consecutive and parallel reactions is still a matter of heated debate. IR spectroscopy,<sup>4</sup> gas chromatography,<sup>3,5</sup> mass spectrometry and NMR spectroscopy 6-10 show that MeOH is initially adsorbed at the framework Brønsted acid sites and then dehydrated to DME. The mixture of MeOH and DME is then converted to alkenes, aliphatics and aromatics up to  $C_{10}$ .

The chemical status of the species in the intracrystalline space in the course of catalytic reactions on molecular sieves can be studied conveniently using <sup>13</sup>C magic-angle-spinning (MAS) NMR spectroscopy.<sup>4,11-17</sup> Reaction rates are of considerable practical importance given the need to be able to predict how quickly a reaction mixture will reach equilibrium and to optimise the rate by the appropriate choice of conditions, such as the pressure, temperature and the nature of the catalyst. We have applied <sup>13</sup>C MAS NMR spectroscopy *in situ*<sup>11,12</sup> to study the kinetics of the first step of this reaction: the conversion of MeOH into DME over an offretite with isomorphous substitution of gallium and/or aluminium for silicon.

The cages of offretite are connected through unrestricted twelve-membered ring apertures in such a way as to form parallel microporous channels *ca*. 6.3 Å in diameter which span the entire length of the crystal in the *c* direction.<sup>18–20</sup> As a result of this arrangement, offretite adsorbs organic molecules of up to 6.0 Å in diameter.

Isomorphous substitution of silicon by a trivalent element such as  $Ga_{,}^{21,22} Al^{23,24}$  or  $B^{25}$  in tectosilicate frameworks creates a net negative framework charge which, for electrical neutrality, must be balanced by a cation. When the cation is a proton, the material exhibits Brønsted acidity. Proton forms of zeolites are prepared by first replacing the charge-balancing cations in the as-prepared material (typically sodium) by the ammonium cation which is then decomposed thermally with the evolution of ammonia gas. The Brønsted site is thus a 'bridging' hydroxy group between Si<sup>IV</sup> and the substituent element, with a dative bond involving a pair of unshared electrons of oxygen and an unoccupied orbital of the substituent element. Gallium-substituted zeolites are known to have lower Brønsted acidity than their aluminosilicate counterparts. Based on the measured IR v(OH) frequencies, Chu and Chang<sup>26</sup> have shown that the Brønsted acidity of the bridging hydroxyl groups increases in the sequence Si(OH) « Ga(OH)Si < Al(OH)Si. On the other hand, offretite is a less powerful catalyst than, for example, zeolites Y and ZSM-5. Nonetheless, it is of considerable interest to catalysis in view of its very different selectivity in a variety of organic reactions.

We are fully aware that the conditions inside a sealed glass microreactor are not the same as those in the flow system which is actually used. Furthermore, given the experimental procedure, the precise pressure inside the microreactor is not known accurately. Alternative procedures, such as magic-angle spinning using <sup>13</sup>C-enriched spinning gas, are totally impracticable in view of the enormous cost involved. With all these reservations, the technique used in this work allows us to monitor *in situ* the evolution of the various products and intermediates in the MTG process, providing information which is unavailable to other techniques, such as gas chromatography (in view of the differential adsorption of MeOH and DME and their different diffusional properties).

### Experimental

#### **Preparation of samples**

Molecular sieves with the offretite structure were synthesized from hydrogels of composition 1.0  $M_2O_3$ : 12 SiO<sub>2</sub>: 1.5  $Na_2O$ : 2.2  $K_2O$ : 4.0 (TMA)<sub>2</sub>O: 250  $H_2O$  (M = Al, Ga; TMA = tetramethylammonium from tetramethylammonium chloride). The required Al/Ga ratio of the gel was obtained by adding a clear aqueous solution of sodium gallate. Crystallization (without stirring) was performed in PTFE-lined Berghoff autoclaves heated at 95 °C for 48 h. The product was washed with distilled water, dried at 100 °C in an air oven, activated by removing the organic templete by calcining at 550 °C for 10 h in air and stored under ambient conditions.

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Powder X-ray diffraction (XRD) indicates that all samples are highly crystalline. Ammonium-exchanged forms of offretite were prepared by repeated treatment of the crystals with a 2 M aqueous solution of NH<sub>4</sub>NO<sub>3</sub> at 60 °C. Finally, the hydrogen forms were made by heating the ammonium-exchanged forms at 500 °C for 4 h in flowing air.<sup>18</sup> XRD, surface area measurements and <sup>29</sup>Si, <sup>27</sup>Al and <sup>71</sup>Ga MAS NMR spectroscopies (results not shown) indicate a decrease of sample crystallinity as a result of the calcination procedure. Some six-coordinate (extra-framework) Al and Ga are generated in the process and the removal of extra-framework Ga is easier than the removal of Al. Microcalorimetry with ammonia as a probe molecule indicates that the insertion of gallium into the aluminosilicate framework results in a heterogeneity of the acid sites: Brønsted acidity is decreased and Lewis acidity increased. The bulk compositions of the three samples of offretite examined in this work are given in Table 1.

For MAS NMR measurements, a small quantity (*ca.* 200 mg) of each catalyst was placed in a Pyrex capsule designed to fit inside a zirconia MAS rotor<sup>27</sup> and the capsule was connected to a vacuum line. The catalyst was activated by heating at 400 °C for 6 h under vacuum, charged with 50 Torr of 30 wt.% <sup>13</sup>C-enriched CH<sub>3</sub>OH at 20 °C and allowed to equilibrate for 1 h before being isolated from the bulk of the gaseous MeOH. The capsule was sealed off under liquid nitrogen to prevent the onset of catalytic processes. The capsule was then heated to the desired reaction temperature, for various lengths of time, quenched and placed in the NMR rotor to record <sup>13</sup>C NMR spectra at ambient temperature.

## NMR spectra

All spectra were recorded on a Chemagnetics CMX-400 spectrometer with zirconia rotors 7.5 mm in diameter, spun at the magic angle at rates of up to 2 kHz in nitrogen gas. <sup>13</sup>C spectra were recorded using high-power decoupling without cross-polarization in order to make the spectra quantitatively reliable. <sup>13</sup>C MAS spectra without proton decoupling and cross-polarization (CP) were also measured. <sup>1</sup>H-<sup>13</sup>C CP MAS NMR spectra were measured only in order to establish whether protons are attached to a given carbon atom or to discriminate between mobile and immobile species. Highpower proton decoupling experiments were carried out with 45° <sup>13</sup>C pulses with a repetition time of 10 s and 300 scans. The longest <sup>13</sup>C  $T_1$  relaxation time is *ca.* 1.5 s, so that a 10 s recycle time is sufficiently long to provide quantitatively reliable spectra. The decoupler was gated off between scans in order to prevent nuclear Overhauser enhancement. Experiments without high-power decoupling used the same acquisition parameters. Cross-polarization spectra were acquired with a 7.3  $\mu$ s proton 90° pulse, a 4 ms contact time and a 4 s repetition time. Chemical shifts are referred to external tetramethylsilane (TMS). Relative concentrations of MeOH and DME were determined by integration of the two well resolved NMR resonances.

## Results

The <sup>13</sup>C MAS NMR spectra of MeOH adsorbed on the three catalysts at room temperature (Fig. 1) and not thermally treated each consist of a single resonance at 50.8 ppm from the methyl groups in adsorbed MeOH.<sup>11,12</sup>



Fig. 1  $^{13}$ C MAS NMR spectra (ppm from TMS) (<sup>1</sup>H decoupling only) of (a) Ga-offretite, (b) Al,Ga-offretite and (c) Al-offretite with 50 Torr of adsorbed CH<sub>3</sub>OH and no thermal treatment

After heating the sample of Ga-offretite at  $150 \,^{\circ}$ C for 40 min the spectrum consists of two lines, at 50.8 and 60.5 ppm [Fig. 2(b)], corresponding to MeOH and DME, respectively. The DME/MeOH concentration ratio is 0.17 and increases when thermal treatment of the sample continues at the same tem-



Fig. 2  $^{13}$ C MAS NMR spectra (ppm from TMS) (<sup>1</sup>H decoupling only) of Ga-offretite heated at 150 °C for (a) 10, (b) 40, (c) 100 min, (d) 3, (e) 4, (f) 5, (g) 7, (h) 10, (i) 12 and (j) 18 h

 Table 1
 Oxide composition (mole ratios) of samples of offretite after ion exchange and calcination

sample	$Al_2O_3$	Ga <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
Ga-offretite Al,Ga-offretite Al-offretite	0.85	1.00 0.15	7.65 7.71 7.79	0.030 0.001 0.033	0.09 0.17

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Fig. 3 <sup>13</sup>C MAS NMR spectra (ppm from TMS) of Ga-offretite with 50 Torr of adsorbed CH<sub>3</sub>OH: (a) heated at 150 °C for 100 min and recorded with proton decoupling only; (b) MAS without proton decoupling; and (c) <sup>1</sup>H<sup>-13</sup>C CP MAS NMR spectrum

perature. Equilibrium is reached after heating for 18 h [Fig. 2(j)], when *ca.* 45% of MeOH has been converted.

With Al,Ga-offretite, dehydration proceeds faster. The DME resonance appears after only 10 min treatment at 150 °C (not shown), and the conversion of MeOH to DME reaches *ca.* 80% after 5 h. With Al-offretite the lines corresponding to DME and MeOH are of comparable intensity after heating at 150 °C for just 20 min, and the reaction is complete within 100 min.

The <sup>13</sup>C MAS NMR spectra with proton decoupling of Al,Ga-offretite [Fig. 3(a)] and Al-offretite (not shown) treated at 150 °C for 40 min reveal a new line at *ca*. 57 ppm which we assign to the DME vapour. We confirmed this assignment as follows. First, we note that the species in question gives rise to a single resonance with a small upfield shift in comparison with that from adsorbed DME. Second, the <sup>13</sup>C MAS spectrum without proton decoupling [Fig. 3(b)] shows that the 57 ppm line is split into a quadruplet with $J_{C-H} \approx 140$  Hz, characteristic of DME.<sup>28</sup> The fact that a spectrum without decoupling can be obtained at all indicates that the species in question is highly mobile. Third, in the spectrum with crosspolarization [Fig. 3(c)] the intensity of the line is considerably lower than the intensity of the line from adsorbed DME, which almost disappears.

We have also found that the MeOH peak moves downfield and its linewidth increases as the concentration of MeOH decreases. We attribute the increased linewidth to a restriction in motion of the adsorbed species, which increases the dipole– dipole and dipole–quadrupole interactions, as well as the chemical shift anisotropy.<sup>29</sup> The downfield shift of the MeOH line is caused by the exchange between adsorbed methoxonium ions and adsorbed methanol<sup>29,30</sup> according to the scheme



(T = Trivalent cation Al or Ga)

in agreement with the mechanism proposed by Anderson and Klinowski<sup>12</sup> who suggested that the first step of the reaction involves protonation of MeOH

$$CH_3OH + HZ \rightarrow (CH_3OH_2)^+ + Z^-$$

where Z stands for the zeolitic framework and the methoxonium ion is a transition structure.<sup>31</sup> The reaction then continues:

$$(CH_3OH_2)^+ + CH_3OH \rightarrow CH_3OCH_3 + H_3O^+$$

# Discussion

As has been shown previously,<sup>11,12</sup> at 150 °C only DME is produced from MeOH when zeolite ZSM-5 is the catalyst. However, while with ZSM-5 the equilibrium between MeOH and DME is approached after heating the sample at 150 °C for 5 min, a much longer period is required when the reaction is carried out over offretite. The difference can be explained in terms of acid strength and shape selectivity as follows.

Zeolite ZSM-5, with a ten-membered ring pore opening, has an effective pore diameter of *ca*. 5.5 Å, whereas the offretite frameworks cages are connected through twelve-membered oxygen rings linked by eight-membered ring apertures leaving parallel channels of *ca*. 6.3 Å in diameter. Shah *et al.*<sup>32</sup> demonstrated that when methanol is situated in the more open cage regions of zeolites, it appears to be unprotonated and less chemically active. It follows that medium-sized pores should be the most active for the MTG reaction because this is where methanol appears to be protonated. Differences in the Brønsted acidity of ZSM-5 and offretite have been assessed by measuring the <sup>1</sup>H NMR chemical shifts of the MeOH hydroxy groups. Anderson *et al.*<sup>19</sup> found a lower acidity of offretite compared to that of ZSM-5.

The percentage of DME formed during the MeOH dehydration, calculated from the intensity (peak area) of the  ${}^{13}C$ MAS NMR resonances vs. the time of reaction t, is plotted in Fig. 4(a). As far as we are aware, this is the first time that the kinetics of MeOH dehydration have been monitored *in situ*. It is clear that the kinetics over the three offretite catalysts of different composition are quite different.

Chang and Silvestri<sup>3</sup> found that, when used as the feed gas, DME is partly converted to MeOH, even in the absence of water. However, below  $200 \,^{\circ}$ C the conversion of DME to MeOH *via* this route is insignificant,<sup>10</sup> and the reaction can be written simply as:

$$2CH_3OH \longleftrightarrow CH_3OCH_3 + H_2O$$

The reaction rate is proportional to the concentration of methanol raised to a power equal to the order of the reaction with respect to that species<sup>33</sup>

$$v = -\frac{1}{2} \frac{d[CH_3OH]}{dt} = \frac{d[CH_3OCH_3]}{dt} = k[CH_3OH]^2$$

where the coefficient k is the rate constant of the reaction, and is independent of the concentration but dependent on the temperature.

The concentration of MeOH has been calculated by assuming that the areas of the individual deconvoluted NMR lines are directly proportional to the populations of the respective chemical species. Fig. 4(b) shows the plot of 1/[MeOH] vs. the duration of the reaction from which the order of the reaction can be obtained. As expected for a second-order reaction, the plot is a straight line in agreement with the integrated form of the second-order rate law:

$$\frac{1}{[MeOH]_t} = \frac{1}{[MeOH]_0} + kt$$



Fig. 4 (a) Percentage of MeOH dehydrated at 150 °C over the three samples of offretite. (b) Plot of 1/[MeOH], vs. reaction time.

Table 2 Kinetics of the conversion of MeOH over the three offretites at 150 °C

	$\frac{Al}{Al + Ga + Si}$	$\frac{Ga}{Al+Ga+Si}$	$k/a.u.^{-1} h^{-1}$
Ga-offretite		0.207	0.045
Al,Ga-offretite Al-offretite	0.175 0.204	0.031	0.863 1.136

a.u. = atomic unit.

where  $[MeOH]_0$  and  $[MeOH]_t$  are the concentration of  $CH_3OH$  at t = 0 and at time t.

The rate constant can be calculated from the slope of the plots. Table 2 gives k for the conversion of MeOH over the three catalysts and the regression coefficients of the corresponding linear equation to which the experimental points have been fitted. The rate constant towards DME increases with increasing aluminium content: 0.045, 0.863 and 1.136 a.u.<sup>-1</sup> s<sup>-1</sup> for Ga-, Al,Ga- and Al-offretites, respectively. We conclude that the rates of formation of DME under different experimental conditions can be determined directly from the NMR spectra and rationalized in terms of acidity and shape selectivity of the individual catalysts.

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