



**Figure 1.** Infrared difference spectra before and after admission of 2 Torr of  $\text{CH}_2=\text{O}$  into FAPO-5 loaded with  $\text{CH}_3\text{OH}$  at 250 K. (a) 2 min, (b) 8 min, (c) 18 min, (d) 60 min, and (e) 90 min after exposure to  $\text{CH}_2=\text{O}$  gas. The weak band at  $1628\text{ cm}^{-1}$  emerging after 60 min is due to  $\text{HCO}_2^-\cdots\text{Fe}$ .

**TABLE 1: Absorption Frequencies of Methanol + Formaldehyde Product in a FAPO-5 Sieve (in  $\text{cm}^{-1}$ )**

reaction product			
$\text{CH}_3\text{OH} + \text{CH}_2=\text{O} \rightarrow \text{CH}_3\text{OCH}_2\text{OH}$	$\text{CH}_3\text{OH} + \text{CD}_2=\text{O} \rightarrow \text{CH}_3\text{OCD}_2\text{OH}$	$\text{CD}_3\text{OD}(\text{H}) + \text{CH}_2=\text{O} \rightarrow \text{CD}_3\text{OCH}_2\text{OD}(\text{H})$	assignment <sup>a</sup>
1412		1415	$\gamma_w(\text{CH}_2)$
	1443 (sh)		
1452	1454		$\delta_a(\text{CH}_3)$
1466	1467		$\delta_a(\text{CH}_3)$
1480		1481	$\delta(\text{CH}_2)$
	2094	2069	$\nu_s(\text{CD}_3)$
	2198		$\nu_s(\text{CD}_2)$
			$\nu_a(\text{CD}_2)$
	2245	2220	$\nu_a(\text{CD}_3)$
			$\nu_a(\text{CD}_2)$
2782		2450 (broad)	$\nu(\text{OD})$
2829	2833	2786	$\nu_s(\text{CH}_2)$
2901			$\nu_s(\text{CH}_3)$
	2911	2901	$\nu_a(\text{CH}_2)$
2938	2938		$\nu_a(\text{CH}_3)$
2966		2966	$\nu_a(\text{CH}_2)$
3000	3002		$\nu_a(\text{CH}_3)$
3280 (broad)	3280 (broad)	3280 (broad)	$\nu(\text{OH})$

<sup>a</sup> Same assignment for more than one product band implies site or Fermi resonance effects.

1, trace a. All bands observed are listed in Table 1, first column. Although growth continues over a period of about 90 min (Figure 1b–e), the product spectrum is already well developed immediately after  $\text{CH}_2=\text{O}$  loading. Hence, the reaction of formaldehyde with methanol is fast compared with the time scale on which the static FT-IR spectra are taken (2 min). The implication is that the reaction has a very low activation barrier. The only product we can conceive of that involves a low activation energy and has no  $\text{C}=\text{O}$  group (no product absorption around  $1700\text{ cm}^{-1}$ ) is methoxymethanol,  $\text{CH}_3\text{OCH}_2\text{OH}$ <sup>4</sup> (the weak, broad band at  $1630\text{ cm}^{-1}$  exhibits an induction period and is due to formate,  $\text{HCO}_2^-\cdots\text{Fe}$ <sup>1</sup>. Its origin will be discussed below). The infrared frequencies shown in column 1 of Table 1 agree with those reported for  $\text{CH}_3\text{OCH}_2\text{OH}$  in the gas phase<sup>5</sup> or isolated in solid Ar.<sup>6</sup> Assignments presented in the last column of Table 1 are based on quantum chemical work reported by Wrobel et al.<sup>6</sup>

The identification of the product as methoxymethanol was confirmed by D isotope labeling experiments. As in the case with the parent isotopes, initial reaction of  $\text{CD}_2=\text{O}$  adsorbed into the FAPO-5 sieve loaded with  $\text{CH}_3\text{OH}$  was too fast for the detection of formaldehyde by static FT-IR spectroscopy. The

resulting product spectrum is shown in Table 1, column 2. Only half as many bands are observed in the CH bending region as in the case of  $\text{CH}_3\text{OCH}_2\text{OH}$ , indicating that the  $1454$  and  $1467\text{ cm}^{-1}$  peaks are due to modes of the  $\text{CH}_3$  group. The three absorptions in the CD stretching region at  $2094$ ,  $2198$ , and  $2245\text{ cm}^{-1}$  are attributed to the  $\text{CD}_2$  group (or Fermi resonance with overtone), and the  $2833$ ,  $2911$ ,  $2938$ , and  $3002\text{ cm}^{-1}$  bands are attributed to stretching modes and Fermi resonances involving overtones of the  $\text{CH}_3$  group of  $\text{CH}_3\text{OCD}_2\text{OH}$ . These assignments, and identification of the product as methoxymethanol, are further corroborated by the spectrum observed upon co-loading of  $\text{CD}_3\text{OD}$  and  $\text{CH}_2=\text{O}$  given in column 3 of Table 1. Upon adsorption of the alcohol (before loading of  $\text{CH}_2=\text{O}$ ), the spectrum of  $\text{CD}_3\text{OD}$  shows bands at  $2076$ ,  $2137$ ,  $2244$ ,  $2500$  (broad), and  $2664\text{ cm}^{-1}$ . The latter two absorptions are assigned to  $\nu(\text{OD})$  of methanol hydrogen bonded to the micropore wall and to free  $\nu(\text{OD})$  of OD groups, respectively. Weaker  $\nu(\text{OH})$  absorptions at  $3250$  and  $3610\text{ cm}^{-1}$  indicate formation of  $\text{CD}_3\text{OH}$  by partial exchange of the OD groups with residual  $\text{H}_2\text{O}$  in the sieve or with lattice OH groups. Upon adsorption of  $\text{CH}_2=\text{O}$ , bands appear in the CH bending region at  $1415$  and  $1481\text{ cm}^{-1}$  and at  $2786$ ,  $2901$ , and  $2966\text{ cm}^{-1}$  in the  $\nu(\text{CH})$  region. Because these are observed in the  $\text{CH}_3\text{OCH}_2\text{OH}$  spectrum, but not in the  $\text{CH}_3\text{OCD}_2\text{OH}$  spectrum, they are attributed to the  $\text{CH}_2$  group. Similarly, the  $2069$  and  $2220\text{ cm}^{-1}$  peaks in the CD stretching region are missing in the  $\text{CH}_3\text{OH} + \text{CD}_2=\text{O}$  product and, hence, are assigned to the  $\text{CD}_3$  group. We conclude that, in a FAPO-5 sieve, formaldehyde adds to methanol to yield methoxymethanol, the hemiacetal being formed in a matter of minutes or faster at 250 K.

Warm up of the sieve to room temperature upon formation of methoxymethanol at 250 K resulted mostly in desorption of the product. Above  $0\text{ }^\circ\text{C}$ , growth of absorptions in the  $\text{C}=\text{O}$  stretching region indicated very slow generation of methyl formate:  $1717\text{ cm}^{-1}$  ( $\text{HCO}_2\text{CH}_3$ ) in the case of  $\text{CH}_3\text{OCH}_2\text{OH}$ ;  $1708\text{ cm}^{-1}$  ( $\text{HCO}_2\text{CD}_3$ ) for  $\text{CD}_3\text{OCH}_2\text{OH}$ ; and  $1685\text{ cm}^{-1}$  ( $\text{DCO}_2\text{CH}_3$ ) in the case of  $\text{CH}_3\text{OCD}_2\text{OH}$ . This process is attributed to dissociation of methoxymethanol to methanol and formaldehyde, followed by Tishchenko dimerization of the aldehyde or Cannizzaro reaction with residual  $\text{H}_2\text{O}$  (as indicated by very slow formation of  $\text{HCO}_2^-$ ) followed by ester condensation with methanol to yield methylformate<sup>1</sup>.

#### Loading of Formaldehyde in the Presence of Water.

Recording of an infrared spectrum immediately following adsorption of 2 Torr of  $\text{CH}_2=\text{O}$  at 250 K into a dehydrated pellet gave the familiar spectrum of formaldehyde in FAPO-5 with peaks at  $1503$ ,  $1732$ ,  $2824$ ,  $2898$ , and  $2990\text{ cm}^{-1}$  reported earlier,<sup>1</sup> as well as residual gas-phase absorptions with Q branches at  $1503$  and  $1745\text{ cm}^{-1}$ .<sup>7</sup> The spectrum is displayed in Figure 2, trace a. As can be seen from trace b, peaks appear within minutes at  $1400$ ,  $1422$ ,  $1472$ , and  $1484\text{ cm}^{-1}$  and also at  $2795$ ,  $2913$ ,  $2978$ , and  $3200\text{ cm}^{-1}$ , with little further growth at later times. Concurrently, all  $\text{CH}_2=\text{O}$  peaks decrease, and a small bleach is observed at  $1650\text{ cm}^{-1}$  coincident with the bending mode of residual  $\text{H}_2\text{O}$  (upon heating of the pellet at  $200\text{ }^\circ\text{C}$  overnight, the residual absorbance of  $\text{H}_2\text{O}$  at  $1650\text{ cm}^{-1}$  is typically 0.15). In addition, the OH stretch absorption of lattice P–OH groups<sup>1</sup> at  $3674\text{ cm}^{-1}$  shows loss of intensity as well (Figure 2). This suggests that both P–OH groups and residual  $\text{H}_2\text{O}$  react with adsorbed formaldehyde. To distinguish the product spectra, a FAPO-5 pellet with a higher concentration of water was prepared by loading 2 Torr of  $\text{H}_2\text{O}$  gas into the sieve after dehydration at  $200\text{ }^\circ\text{C}$ . The additional increase of the  $\text{H}_2\text{O}$  bending mode intensity was 0.1 absorbance units. A