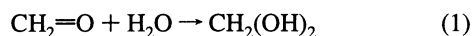


Figure 2. Infrared difference spectra recorded upon adsorption of 2 Torr of $\text{CH}_2=\text{O}$ on a FAPO-5 sieve at 250 K (a) immediately after loading and (b) 3 min later. Trace c shows the infrared difference spectrum recorded upon adsorption of 1.3 Torr $\text{CH}_2=\text{O}$ onto a FAPO-5 sieve loaded with 2 Torr H_2O after dehydration of the pellet.

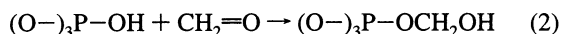
TABLE 2: Absorption Frequencies of Adducts of Formaldehyde with H_2O and Lattice P-OH Groups in a FAPO-5 Sieve (in cm^{-1})

reaction product		assignment
$\text{CH}_2=\text{O}$ loading	$\text{CD}_2=\text{O}$ loading	
1400		$\gamma_w(\text{CH}_2)$, POCH_2OH
1425		$\gamma_w(\text{CH}_2)$, $\text{CH}_2(\text{OH})_2$
1470		$\delta(\text{CH}_2)$, POCH_2OH
1483		$\delta(\text{CH}_2)$, POCH_2OH
	2105	$\nu_s(\text{CD}_2)$, POCD_2OH
	2138	$\nu_s(\text{CD}_2)$, $\text{CD}_2(\text{OH})_2$
	2225 (sh)	$\nu_a(\text{CD}_2)$, POCD_2OH
	2254	$\nu_a(\text{CD}_2)$, $\text{CD}_2(\text{OH})_2$
2796		$\nu_s(\text{CH}_2)$, POCH_2OH
2912		$\nu_a(\text{CH}_2)$, POCH_2OH
2980		$\nu_a(\text{CH}_2)$, $\text{CH}_2(\text{OH})_2$
3200 (broad)	3200 (broad)	$\nu(\text{OH})$, $\text{CH}_2(\text{OH})_2$, POCH_2OH $\text{CD}_2(\text{OH})_2$, POCD_2OH

difference spectrum taken immediately after addition of 1 Torr $\text{CH}_2=\text{O}$ into this matrix, shown in Figure 2c, exhibits the same product bands as those observed in trace b. Depletion of H_2O around 1650 cm^{-1} and of $\nu(\text{OH})$ of P-OH groups at 3674 cm^{-1} again indicates that both H_2O and lattice hydroxyl groups interact with formaldehyde. Product bands at 1425 and 2980 cm^{-1} are more intense in the spectrum in Figure 2 part c than those in part b, however. Hence, they are assigned to $\text{CH}_2(\text{OH})_2$, the expected reaction product of H_2O and $\text{CH}_2=\text{O}$:



Indeed, the two bands agree well with the infrared spectrum of methanediol isolated in solid Ar.⁸ All other product absorptions (except 1676 cm^{-1} , see below) are attributed to the addition product of $\text{CH}_2=\text{O}$ and lattice OH groups



Bands assigned to P-OCH₂OH agree well with literature values for CH_2 stretching and bending modes of P-O-CH₂ moieties.⁹ Frequencies and assignments of the reaction products of $\text{CH}_2=\text{O}$ with H_2O and P-OH are summarized in column 1 of Table 2. It is important to note that the infrared spectra assigned here to $\text{CH}_2(\text{OH})_2$ and POCH_2OH are similar to those of surface bound dioxymethylene and polyoxymethylene compounds observed when adsorbing gaseous $\text{CH}_2=\text{O}$ onto various porous oxides.^{10,11} This is not surprising because all these species feature the same OCH₂O moiety.¹² However, the formaldehyde products

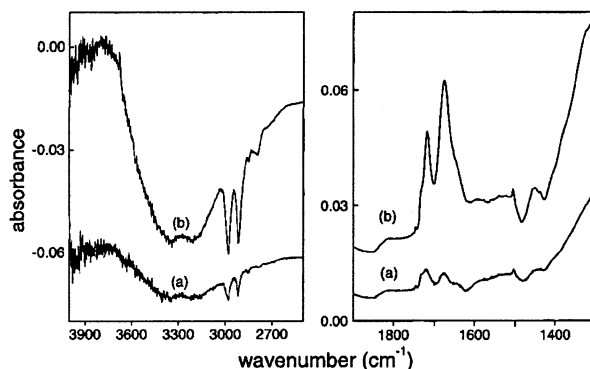


Figure 3. Thermal behavior of adducts formed upon coadsorption of $\text{CH}_2=\text{O}$ and H_2O in FAPO-5. Infrared difference spectra show reaction after the warming of the system displayed in Figure 2c to 296 K: (a) immediately after reaching 296 K and (b) 70 min at 296 K.

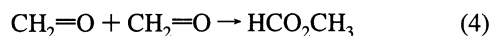
observed on oxide surfaces can be distinguished from those found in the FAPO-5 sieve based on their thermal stability; the oxymethylene species formed on porous oxide surfaces are stable at room temperature, whereas $\text{CH}_2(\text{OH})_2$ and POCH_2OH quantitatively dissociate above $0 \text{ }^\circ\text{C}$ (see below).

Analogous loading experiments with $\text{CD}_2=\text{O}$ confirmed the result with the parent reactions just described. In “dehydrated” FAPO-5 (no extra water added after evacuation at $200 \text{ }^\circ\text{C}$) or in FAPO-5 loaded with an additional small amount of H_2O , both gas phase (1701 cm^{-1}) and adsorbed $\text{CD}_2=\text{O}$ (1685 , 2091 , 2213 , 2256 cm^{-1}) decreased rapidly under depletion of H_2O and lattice OH groups. Product absorptions were at 2105 , 2138 , 2225 (shoulder), and 2254 cm^{-1} . Comparison of the product intensities at the two H_2O concentrations indicates that the 2138 and 2254 cm^{-1} peaks originate from $\text{CD}_2(\text{OH})_2$, in good agreement with a Raman study of $\text{CD}_2(\text{OD})_2$,¹³ whereas 2105 and 2225 cm^{-1} absorptions are assigned to C-D stretching modes of P-OCD₂OH groups (Table 2, column 2). The OH stretching modes of both products give rise to a broad absorption around 3200 cm^{-1} .

Warm up to 296 K of the FAPO-5 sieve containing $\text{CH}_2(\text{OH})_2$ and P-OCH₂OH led to depletion of the two adducts under release of $\text{CH}_2=\text{O}$ (1504 , 1732 cm^{-1}). Figure 3a shows the infrared difference spectrum taken after and before raising the pellet temperature from 250 to 296 K for FAPO-5 preloaded with an additional amount of H_2O . After 70 min at 296 K , nearly quantitative conversion of $\text{CH}_2(\text{OH})_2$ to methyl formate, HCO_2CH_3 (1717 , 1456 , and 1436 cm^{-1}) and HCO_2H (1679 and 1381 cm^{-1}), has occurred (Figure 3b). Assignments of these products are readily made on the basis of FT-IR measurements reported earlier for room-temperature loading of CH_2O .¹ The emergence of formaldehyde suggests that the initial step upon warm is the reverse of reactions 1 and 2 followed by Cannizzaro disproportionation:^{1,14}



We have noted previously that formic acid and methanol condense slowly to methylformate in a FAPO-5 sieve at room temperature.¹ Because the growth of HCO_2CH_3 in Figure 3 does not exhibit a clear induction period, the ester may in addition emerge from Tishchenko dimerization of formaldehyde^{15,16}



Note that a very small amount of HCO_2H is already formed upon $\text{CH}_2=\text{O}$ loading at 250 K (Figure 2c). However, the growth of these bands at 250 K shows a distinct induction