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Polymerization with Zeolite Catalysts

II. Vinyl Ethers Over H-Mordenite and H–Y

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Ethylvinyl, *n*-butylvinyl and isobutylvinyl ethers all react readily over H-mordenite and H-faujasite (H–Y) near room temperature to produce low molecular weight polymers. Over H-mordenite all follow the kinetic relation,

$$Q_t = k(t)^{1/2} + \gamma,$$

where Q_t is the mass uptake at constant pressure p and time t. k and γ are coefficients. Over H–Y the kinetics followed the Elovich equation

$$Q_t = k \ln t + \gamma.$$

Over both catalysts the rate coefficients were linear functions of pressure, i.e., $k = (ap + b)$ where a and b are coefficients. As shown previously for *n*-butylvinyl ether over H-mordenite [Barrer, R. M., and Oei, A. T. T., *J. Catal.* 30, 460 (1973)], water in small amounts was also a co-catalyst for polymerization of the same vinyl ether over H–Y. The kinetics have been interpreted as indicating that little polymer forms within the channels of mordenite but that within those of faujasite considerable polymer forms and progressively blocks intracrystalline sites. Supporting evidence of this has been obtained by water sorption in and thermogravimetric analyses of zeolite + polymer composites.

INTRODUCTION

In an earlier paper (*1*) the polymerization of *n*-butylvinyl ether was studied over a H-mordenite catalyst. The reaction occurred readily near room temperature to give low molecular weight polymers. It was of interest to extend this study to other vinyl ethers and to compare H-mordenite and H-faujasite (H–Y) catalysts. It was an objective of the investigation to prepare zeolite–polymer composites in which, by *in situ* reaction, the adhesion between polymer and zeolite filler is improved by complete wetting of filler by the growing polymer films. If intracrystalline polymerization occurred, polymer chains threaded into the zeolite channels should enhance the adhesion between polymer outside the crystal and the crystal. In this respect the three-dimensional network of channels in zeolite Y may behave differently from the parallel channels in mordenite.

EXPERIMENTAL METHODS

The monomers used were ethyl-, isobutyl- and *n*-butylvinyl ethers. Polymerization was followed gravimetrically using silica spring balances (*1*). In each balance about 0.1 g of catalyst was outgassed for 7 days at temperatures rising to 360°C. Kinetic runs were performed at 30°C at each of several constant vapor pressures.

Sorption of water by the pure catalysts and by catalyst–polymer composites was also measured gravimetrically, after outgassing at 30°C for 8 hr to remove residual

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monomer. Composites in much larger amounts were prepared for molecular weight determinations and thermogravimetric analyses (tga). Cone-shaped containers with several grams of catalyst were suspended in the balance cases and outgassed as indicated for the kinetic runs. Polymerizations were then effected at 30°C at vapor pressures of 17.5, 1.26 and 2.28 cm Hg for ethyl-, *n*-butyl- and isobutylvinyl ethers, respectively. After 5 hr the polymerizations were stopped and the composites were removed. Polymer was then extracted with $CHCl_3$ and the solvent plus any dissolved monomer were subsequently removed by evacuation. Molecular weights of polymers were determined with a Hewlett-Packard vapor pressure osmometer (Type 300-B) using $CHCl_3$ as solvent.

In preparation for tga the catalyst crystals with any residual polymer remaining from the treatment of the previous paragraph were extracted a further five times with $CHCl_3$, filtered, washed again five times with $CHCl_3$ and dried. The crystals were then equilibrated over saturated Na_2SO_4 (water vapor pressure at 20°C = 1.60 cm Hg). In tga runs the temperature was programmed to rise at 20°C/min to 600°C or more.

By electron microscopy the cylinder-shaped H-mordenite crystals were found to have average diameters and lengths of 4.2 and 4.6 μm, respectively, and the cubic crystals of H–Y had average edge lengths of 1.35 μm. The H-mordenite was available as H-Zeolon. The H–Y was prepared from Na–Y by the reactions

$$\underset{(100\text{ g})}{\text{Na–Y}} \xrightarrow[1\text{ day}]{4.24\,M\ \mathrm{NH_4Cl}(250\text{ ml})} \mathrm{NH_4}\text{–Y} \xrightarrow[3\text{ days in air}]{360°\mathrm{C}} \text{H–Y}.$$

RESULTS AND DISCUSSION

Kinetics. Polymerization of the vinyl ethers occurred readily over both H-mordenite and H–Y. Over H-mordenite the fractional weight increase, Q_t, (g/g of dry zeolite), obeyed the same $(t)^{1/2}$ law for ethyl- and isobutylvinyl ethers as was observed for *n*-butylvinyl ether (*1*):

$$Q_t = k(t)^{1/2} + \gamma, \tag{1}$$

where k and γ are coefficients. The validity of Eq. (1) is shown by Fig. 1a and b. The coefficients k were in turn linear functions of pressure as shown by Fig. 1c. Thus these two vinyl ethers repeat closely the kinetics observed with *n*-butylvinyl ether over H-mordenite (*1*). In the relation,

$$k = ap + b, \tag{2}$$

which is illustrated in Fig. 1c the coefficient b would be expected to be zero since there is no reaction when $p = 0$. These values of b are not zero, however, and this could mean that at the lowest pressures the straight line relation of Eq. (2) no longer applies. A further resemblance of the kinetics of polymerization of ethylvinyl and isobutylvinyl ethers with *n*-butylvinyl ether (*1*) is that for $Q_t \sim 0.6$, which is in the region where the polymer films first become visible, the curves of Q_t vs $(t)^{1/2}$ show breaks followed by slower polymerisation. Q_t, however, still tended to follow a $(t)^{1/2}$ relation of lower slope. This suggests partial coalescence of polymer films growing on neighboring crystals, under surface tension forces, once a certain amount of polymer has formed If diffusion of monomer through the films partially [though not wholly (*1*)] controls the kinetics then film coalescence will modify the average lengths of the diffusion paths involved in reaching the catalytic centers. At constant pressure at the external surfaces of the growing polymer films the rate of transport to the crystal surfaces could then vary in a linear manner with pressure in accord with Eq. 2. Even if the rate controlling step were chemical reaction at the catalytic sites this rate could still be proportional to the pressure.

With H–Y as catalyst the above three vinyl ethers polymerized according to a different kinetic law from Eq. (1). Q_t now tended to be a linear function of ln t. as shown in Fig. 2a. Thus the rate equation has the form

$$Q_t = k \ln t + \gamma \tag{3}$$

where k and γ are coefficients. At constant pressure Eqs. (1) and (3) have the general differential form

$$\frac{dQ_t}{dt} = \frac{\text{constant}}{t^n}, \qquad (4)$$

where $n = \frac{1}{2}$ over H-mordenite and $n = 1$ over H-Y. Equation (3) has the form of the Elovich equation (*2*, *3*) which requires the rate of reaction to decay according to an exponential function of the amount of reaction which has already occurred:

$$\frac{dQ_t}{dt} = \frac{k}{t} = kc\,\exp(-Q_t/k), \qquad (5)$$

where $c = \exp(\gamma/k)$. This equation also describes the kinetics of reaction of tetramethylsilane (TMS) with H-Y (*4*), in which $\equiv$Si—OH groups progressively react with TMS and evolve methane. In the context of polymerization over H-Y an explanation of Eq. (3) could be that catalytic centers in H-Y are progressively inactivated by polymer growth. This could be a result of formation of immobilized polymer clogging the intracrystalline channel system of H-Y more and more so that access of monomer to intracrystalline sites becomes increasingly difficult. On the other hand if over H-mordenite little or no immobile intracrystalline polymer forms only surface sites can be active and monomer can always displace polymer segments on an external surface and so reach active sites. Further evidence on this interpretation of the distinctive kinetics over H-Y

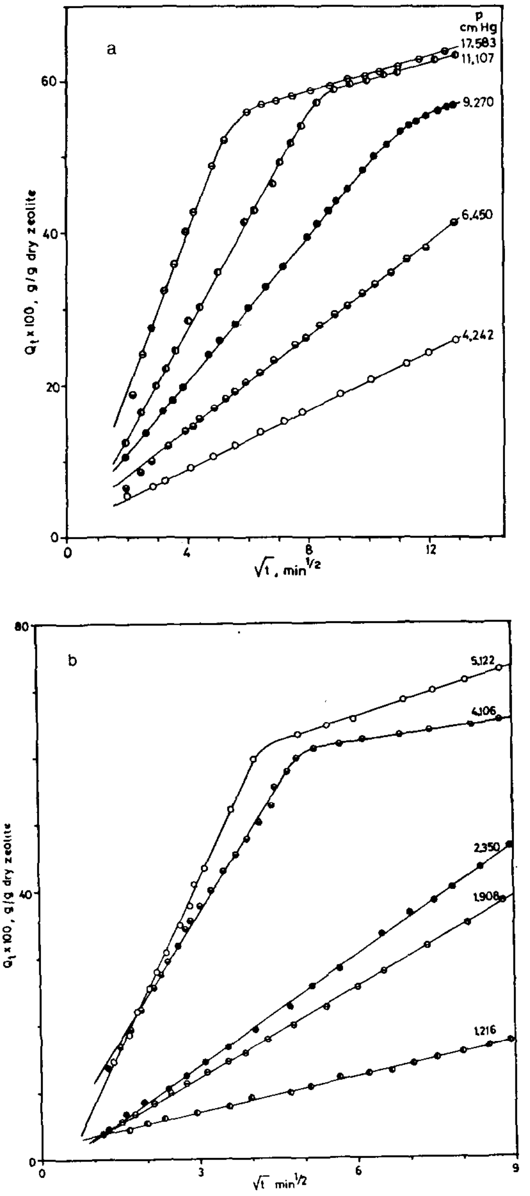

FIG. 1a. The weight increase, Q_t, in grams per gram of outgassed H-mordenite plotted against $(t)^{1/2}$ for ethylvinyl ether. (b) Q_t against $(t)^{1/2}$ for isobutylvinyl ether. (c) The rate coefficients k as functions of pressure for polymerisation of ethylvinyl (○) and isobutylvinyl (●) ethers.

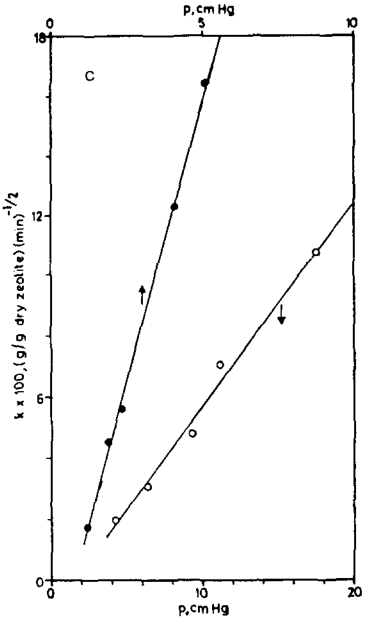

FIG. 1c.

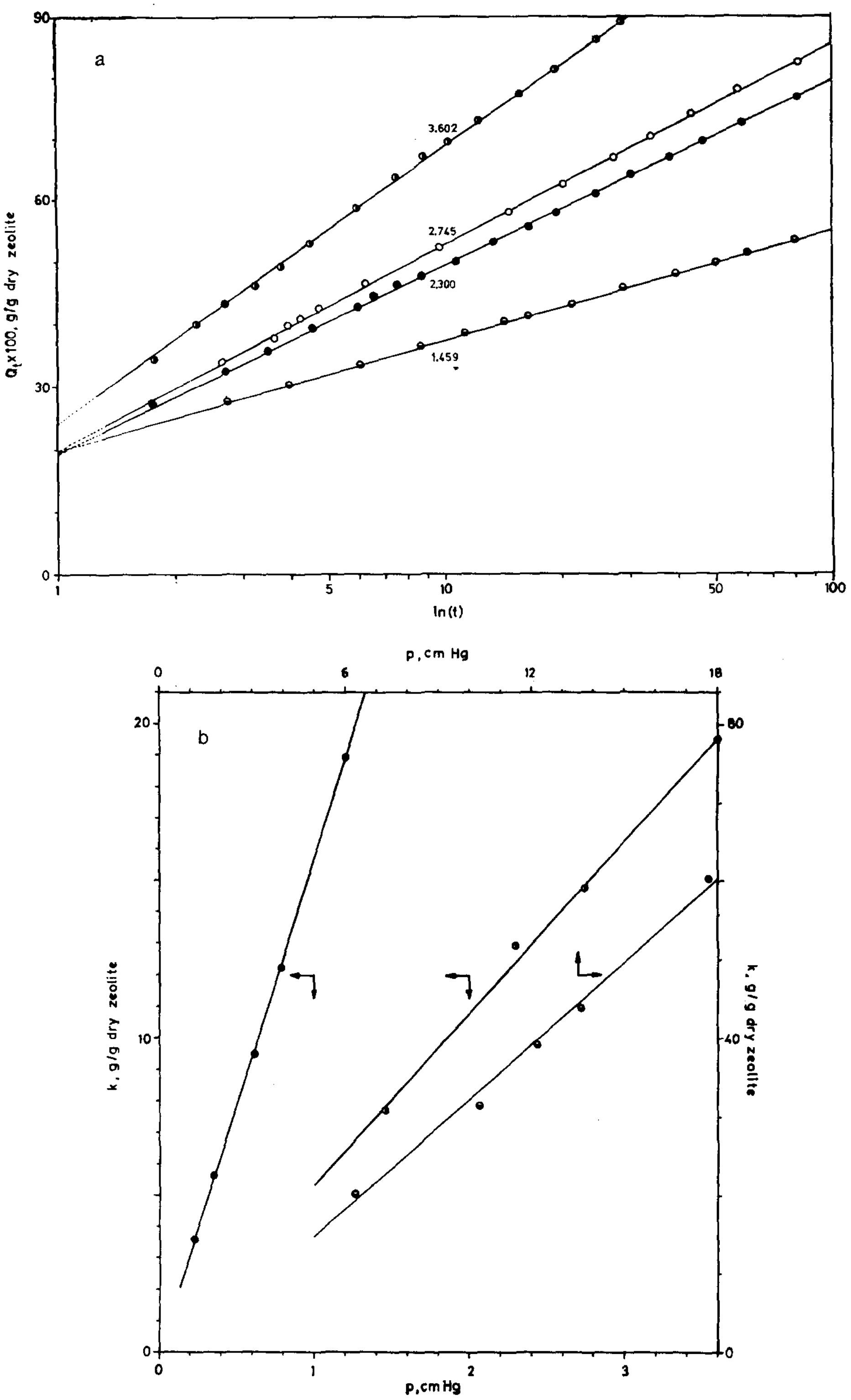

FIG. 2a. Q_t plotted against ln t (t in min). The numbers on the curves are the constant vapor pressures of isobutylvinyl ether. The runs were made with H-Y at 30°C. (b) Plots of k vs pressure of monomer vapor for ethylvinyl (◒), isobutylvinyl (◑) and n-butylvinyl (●) ethers.

TABLE 1

COEFFICIENTS a^a IN THE RELATION $k = ap + b$, AND $a' = a/M$ (M = MOLECULAR WEIGHT OF POLYMER), AND THE PARAMETERS σ^* AND E_s FOR THE GROUPS R IN R—O—CH=CH$_2$

Catalyst	R	10^2a	$10^4a'$	σ^*	E_s
H-mordenite	C_2H_5–	0.68	0.94	−0.100	−0.07
[Eqs. (1) and (2)]	iso-C_4H_9–	3.7_4	3.7_4	−0.125	−0.93
	n-C_4H_9–	10.2	10.2	−0.130	−0.39
H-Y	C_2H_5–	3.5_1	4.8_7	−0.100	−0.07
[Eqs. (3) and (2)]	iso-C_4H_9–	5.4	5.4	−0.125	−0.93
	n-C_4H_9–	15.7	15.6	−0.130	−0.39

[a] The units for a in Eq. (1) are grams per gram of dry zeolite per cm Hg per min$^{1/2}$, and those of a' in Eq. (1) are moles per gram of dry zeolite per cm Hg per min$^{1/2}$. Those of a and a' in Eq. (3) are, respectively, grams per gram of dry zeolite per cm Hg and moles per gram of dry zeolite per cm Hg.

as compared with H-mordenite is presented later from water uptake and from tga curves.

The coefficients k in Eq. (3) were, like the k in Eq. (1), linear functions of pressure, as shown in Fig. 2b. The coefficients a of Eqs. (1) and (2) are given in Table 1 together with the corresponding coefficients.

$$a' = \frac{a}{M}, \tag{6}$$

where M is the molecular weight of the monomer. In Table 1 are also included the polar substituent and steric substituent Taft parameters, (*5, 6*), σ^* and E_s, respectively. The a and a' increase in the sequence ethyl < isobutyl < n-butyl, which is also the sequence of the electron donating ability of the alkyl groups as measured by the negative values of σ^*. On the other hand the parameter E_s does not change regularly with the rate coefficients a, which may indicate that molecular size of the alkyl group is not a controlling factor. The correlation between a and σ^* supports the carbonium ion mechanism proposed earlier and further implies that the kinetics over H-mordenite are not wholly diffusion controlled, despite the form of Eq. (1).

The influence of zeolitic water. When n-butylvinyl ether polymerized over H-mordenite containing increasing amounts of zeolite water the initial reaction rates at first increased but then at high water content declined again (*1*). The influence of water upon the rate of polymerization of n-butylvinyl ether over H-Y is shown in Fig. 3a. Small amounts of water increase the slope of the linear part of plots of Q_t vs ln t. For large amounts of water the rates are initially much depressed but then, as over H-mordenite (*1*), show progressive acceleration, possibly due to displacement of some water by monomer and polymer as reaction proceeds. If the initial slopes of the curves of Q_t vs ln t [i.e., the values of k in Eq. (3)] are plotted against the amount of water the curve passes through a maximum near 5% uptake of water (g/g of dry zeolite). Thus in small amounts water functions as a co-catalyst with H-Y as with H-mordenite. The strong variation of the rate of polymerization with water content provides further evidence that the kinetics are at most only partially con-

TABLE 2

NUMBER AVERAGE MOLECULAR WEIGHTS OF POLYMERS GROWN AT 30°C FROM R—O—CH=CH$_2$

Catalyst	R–	Pressure of monomer (cm Hg)	MW of polymer	Monomer units in polymer
H-mordenite	C_2H_5–	17.5	540	8
	iso-C_4H_9	2.28	1700	17
	n-C_4H_9	1.26	990	10
H-Y	C_2H_5–	17.5	480	7
	iso-C_4H_9	2.28	1100	11
	n-C_4H_9	1.26	630	6

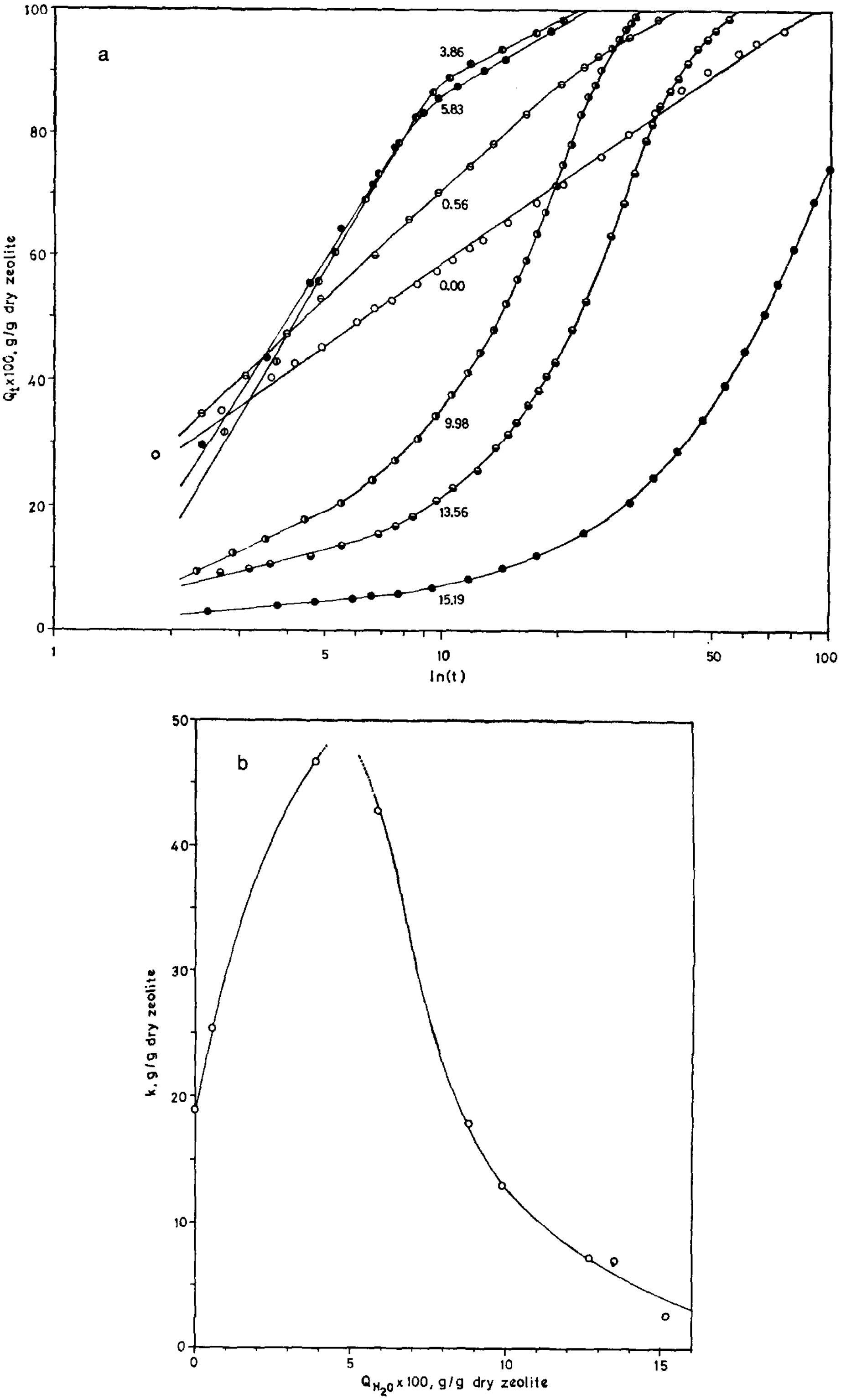

FIG. 3a. Q_t plotted against ln t [t (min)] for n-butylvinyl ether at 30°C over H–Y, after sorption of water in wt% given by the numbers on the curves. (b) The initial values of the coefficients k of Eq. (3) for the curves of Fig. 3a plotted against the wt% of sorbed water.

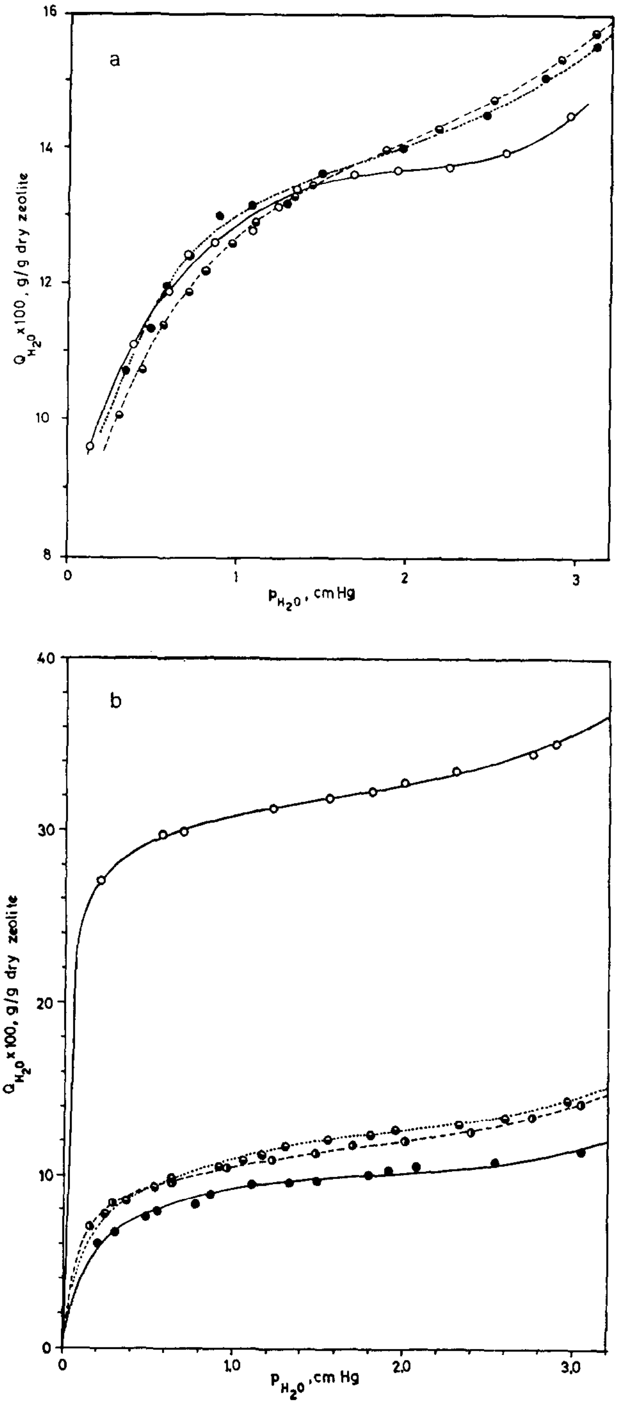

FIG. 4a. Isotherms for sorption of water at 30°C in pure H-mordenite (○), in H-mordenite + 20.7% by wt of poly(ethylvinyl ether) (◒) and in H-mordenite + 9.7% by wt of poly(isobutylvinyl ether) (●). (b) Isotherms for sorption of water at 30°C in pure H-Y (○), in H-Y + 24.3% by wt of poly(ethylvinyl ether) (◒), in H-Y + 29.3% of poly(isobutylvinyl ether) (◑) and in H-Y + 27.6% of poly(*n*-butylvinyl ether) (●).

trolled by the rate of diffusion of monomer through polymer films growing around each catalyst crystal.

Molecular weights of polymers. The number average molecular weights of the vinyl polymers formed over H-mordenite and H–Y are given in Table 2. All the polymers grown at 30°C are of low molecular weight. When monomer molecules reach a catalyst site they may either react with the terminal group of a polymer chain or they may initiate a new polymer chain by reaction with a second monomer molecule. Evidently initiation of new polymer chains replaces chain growth when the polymer is still of limited length. The effect of temperature upon chain length is still to be investigated, but the length would be expected to increase as the reaction temperature is lowered.

Water sorption isotherms. Isotherms for water uptake by pure H-mordenite and by H-mordenite–polymer composites with 20.7 and 9.7 wt% of poly(ethylvinyl ether) and poly(isobutylvinyl ether), respectively, are shown in Fig. 4a. Water uptake in the polymer is expected to be very small and so the uptake of water within the mordenite crystals is little affected by the polymer. Therefore the amount of polymer formed and retained within the mordenite crystals must be small, especially for poly(isobutylvinyl ether).

With H–Y the water uptake behaves very differently. Sorption isotherms are shown in Fig. 4b for H–Y and H–Y–polymer composites in which the wt% was, respectively, 24.3, 29.3 and 27.6 with respect to outgassed zeolite for poly(ethylvinyl ether), poly(isobutylvinyl ether) and poly(*n*-butylvinyl ether). When the greatly reduced water uptakes were compared with that in pure H–Y it was estimated that about 62, 64 and 69% of the intracrystal-

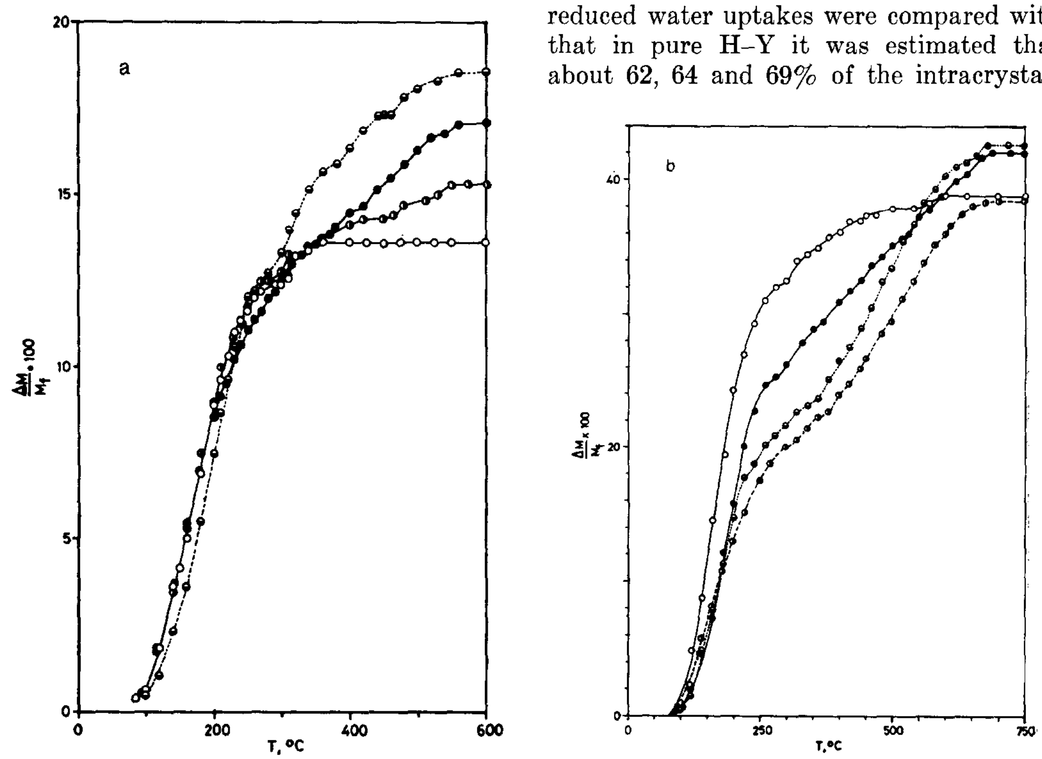

FIG. 5a. Thermogravimetric weight loss (% of final wt at 600°C) for pure H-mordenite (○), and composites with poly(isobutylvinyl ether) (◑), poly(*n*-butylvinyl ether) (●) and poly(ethylvinyl ether) (◒). (b) Thermogravimetric weight loss curves (% of final wt at 750°C) for pure H–Y (○) and for composites with poly(ethylvinyl ether) (◒), poly(isobutylvinyl ether) (◑) and poly(*n*-butylvinyl ether) (●). In (a) and (b) the polymer in the composites was that which could not be removed from the zeolite by extraction with $CHCl_3$.

line pore volume of H–Y was inaccessible to water for the three composites in the order given above. It was inferred from this that in H–Y polymerization occurred at sites within the crystals, whereas with H-mordenite polymerization was largely confined to the external surfaces of the crystals.

Thermogravimetric analyses. The thermogravimetric analyses were made on zeolite–polymer composites from which as much as possible of the polymer had been removed with $CHCl_3$ as described in the experimental section. The curves of weight loss, ΔM, relative to the final mass, M_f, are shown, respectively, in Figs. 5a and b for H-mordenite alone and H-mordenite + polymer and also for H–Y alone and H–Y + polymer. Since in the mordenite systems of Fig. 4a the water contents are similar in mordenites with and without polymer the same should apply to the water contents of the mordenites in Fig. 5a. Accordingly the amounts of polymer which were not removed by $CHCl_3$ extraction can be estimated as the limiting weight loss of pure H-mordenite subtracted from those of the mordenite + polymer composites. The amounts so estimated are 1.8, 3.5 and 5% of the weights of dry zeolite for the polymers from isobutyl-, *n*-butyl- and ethylvinyl ether, respectively. These could represent upper limits to amounts of polymer entrained in the intracrystalline channels.

The water contents of H–Y, and of H–Y + polymer given in Fig. 4b give estimates at 1.4 cm Hg of 11.8, 11 and 9.5 wt% of water in the dry zeolite for zeolite + polymer composites in which the polymer was obtained from ethyl-, isobutyl- and *n*-butylvinyl ether, respectively. The tga curves of Fig. 5b for the composites H–Y + unextractable polymer show breaks above 250°C which suggest that here the onset of oxidative removal of polymer supersedes the near-termination of zeolitic water loss. For zeolitic + hydroxyl water rough estimates from these curves and that of pure H–Y are 29, 26 and 24%, rather more than for the zeolitic water only of the unextracted samples of Fig. 4b but much less than ~39% total loss from pure H–Y shown in Fig. 5b. If these estimates are subtracted from the total weight losses of the composites of Fig. 5b one finds 14, 16 and 15% of unextractable polymer from ethyl-, *n*-butyl- and isobutylvinyl ethers, respectively (at 750°C all organic matter was burnt away and the crystals were quite white). These figures indicate, in line with the water sorption (Fig. 4b) that polymer inclusion complexes form more readily with H–Y than with mordenite. This may be a general tendency with sufficiently open three-dimensional channel networks compared with crystals having parallel nonintersecting channels. A second factor is the smaller intracrystalline free volume in H-mordenite than in H–Y.

CONCLUSION

For the three vinyl ethers considered in this work the kinetic results, the water sorption and the thermogravimetric measurements are all consistent with the conclusion that not much intracrystalline polymer forms in H-mordenite crystals, but that considerable intracrystalline polymerization occurs in the channels in H–Y. Even with H-mordenite, however, since not all the polymer was removed with $CHCl_3$, there must be good adhesion between this residual polymer and the crystals. Adhesion to H–Y should be even better judging from the amounts of polymer unremoved by extraction with $CHCl_3$. H–Y catalyst in particular can therefore be envisaged as filler in polymer–catalyst composites in which there should be complete wetting of filler by polymer chains, some of which are laced into the channels of H–Y and may also be entangled with the chains of bulk polymer. Catalyst filler particles may be coated with partially unremovable vinyl polymer by the catalyzed polymerization, and then mixed with the same or another bulk polymer or with other monomers plus accelerators, to yield polymer–filler composites. It seems therefore that objectives referred to in the introduction should be realizable.

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