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The Effect of O_2 on the Thermal Activation of Zeolite Beta

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The process of converting "as-synthesized" zeolites which contain organic templating agents generally begins by calcining the material to remove the organic material. Most often, this initial calcining step is performed in the presence of O_2 which is thought to help burn out residue which forms during the thermal breakdown of the organic template. We have discovered that O_2 promotes the formation of residue from tetraethylammonium ions in zeolite beta (BEA), probably by participating directly in a polymerization process. This discovery has also been extended to tetrapropylammonium ions in MFI and to simple amine adsorbates such as 1-propanamine adsorbed on acid sites in both BEA and MFI. We therefore believe that this is a general rule which may be applied to all amine templates in zeolites.

A more efficient route to organic template removal is to first calcine the material in the absence of O_2 so that the polymerization process which involves O_2 is suppressed. This results in a material which has only a trace of residue which can be removed by heating briefly in O_2 at a moderate temperature. Materials initially calcined in O_2 require either a lengthy treatment at a moderate temperature or a shorter treatment at a higher temperature to completely remove the residue. © 1996 Academic Press, Inc.

INTRODUCTION

Zeolite Beta (BEA) is a large pore, high silica zeolite which is generally synthesized in the presence of the tetraethylammonium (TEA) cation. The BEA structure was first reported in 1988 as a highly faulted intergrowth of two distinct but closely related structures termed polymorphs A and B (1). Both polymorphs of BEA consist of straight 12-membered ring channels along *a* and *b* having elliptical cross sections of about 6.0 × 7.3 Å and 6.8 × 7.3 Å for polymorphs A and B, respectively. In the *c* direction, a tortuous 12-membered ring channel results from faulting, and it has a nearly circular cross section of about 5.5 Å.

Even though BEA was first described in a patent filed in 1964 (2), its usefulness as a catalyst for hydrocarbon conversion reactions such as cracking, hydrocracking, dewaxing, and dealkylation was not widely reported until almost 20 years later. Corma *et al.* (3), for example, concluded that BEA has a higher potential for alkylation reactions because of a lower hydrogen transfer activity and slower catalytic activity decay than H–Y with a similar Si/Al ratio. Since the framework Si/Al ratio is a controlling factor in virtually all acid catalyzed reactions on zeolites, many research efforts have been focused on this physical property of BEA. Acidic -OH groups associated with framework Al have been detected at 3615 (4, 7), 3602 (5, 6), and 3606 cm^{-1} (8) and acid strengths followed the order ZSM-5 > BEA > Y (5) and BEA > ZSM-20 ≥ Y (6). One study reported that dealumination by acid leaching increases the acid strength of sites in BEA (8) as generally observed in other zeolitic systems but another report (6) found that the turnover frequency for *n*-hexane cracking is constant with the framework Al content of BEA. Also, a recent study of 2-propanamine cracking over BEA (9) found that not all framework Al sites are associated with an acidic site.

Several studies deal with the synthesis of BEA in the aluminosilicate form (10–12), and isomorphously substituted gallium (13–15), boron (16), titanium (17) and iron (18) analogs. TEA plays a crucial role in the synthesis process as both a framework charge compensating cation and a pore-filling organic "template." To completely fill the pores of BEA, six molecules of TEA per tetragonal unit cell are required (12), so a "stoichiometric" TEA–BEA contains six framework Al atoms per unit cell charge compensated by six molecules of TEA. In this paper, we disclose an unexpected effect related to the O_2 content of the calcining atmosphere which we have observed during thermal treatment of TEA–BEA. This template removal process is recognized as a very important step in the production of quality sorbents and catalysts. Thermal treatment in an O_2-containing atmosphere at a final temperature high enough to ensure complete combustion of organic template is apparently the preferred activation procedure for many zeolites including BEA. Reported conditions for BEA include a flow of dry air at 723 K for 20 h (5), calcination at 813 K for 15 h (6) (presumed to be in air), calcination in air at 773 K for 5 h (7), calcination at 823 K for 6 h with air diluted in N_2 (8) (actual O_2 content not given), flow of dry air at 700 K for 24 h (14), calcination at 823 K overnight (15) (presumed to be in air), ultra high purity O_2 at 773 K for 5 h (19), and calcination in dry air for 6 h at temperatures ranging

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from 833–1273 K (20). Our past procedures for calcination of as-synthesized zeolites which contain organic templates involved treatment in 3–5% O_2 in an inert gas (He, Ar, or N_2) at 823–873 K and we arrived at these conditions through informal discussions are collaborations with several prominent zeolite researchers. The low O_2 content was designed to minimize possible thermal runaway or explosion due to ignition of the organic template or volatile decomposition products. We have found mention of thermal treatment of BEA in an O_2-free environment in only two papers (9, 21), but neither of these were suggested in the context of calcination of bulk quantities of material or as a viable activation procedure. Two examples of calcination of zeolites in an O_2-free environment followed by treatment in an O_2-containing environment (which we find particularly advantageous as we report here) can be found in the MFI system (22) and more generally for $AlPO_4$'s (23).[2] An explanation of their methodology was not given by Schwarz *et al.* (22) but the patent by Chu and Beck (23) explains their methodology as preserving the structural integrity of the $AlPO_4$'s.

Thermal analysis (TA) has been widely applied to the study of organic template removal from many zeolites (24, 25) and zeolite precursors (26). In the case of BEA, most TA studies we have uncovered were performed in flowing air (5, 12, 14, 17) but Perez-Pariente *el al.* report one experiment performed in N_2 along with numerous samples observed in flowing air (21). Four primary regions are generally observed in the DTA spectra resulting from such experiments on BEA, and when interpreted in light of early work on TEA–MFI, the following assignments have been made (25):

Peak I	298–400 K	zeolitic water loss
Peak II	400–623 K	decomposition of occluded TEA–OH
Peak III	623–773 K	decomposition of zeolitic TEA cations
Peak IV	773–973 K	decomposition of TEA residues strongly adsorbed on acid sites.

A reasonable estimate of the total TEA content is therefore the weight loss associated with Peaks II + III + IV while zeolitic TEA cations can be estimated from the weight loss associated with Peaks III + IV. TEA decomposition has also been studied with a combined TA–MS technique, and sequential Hofmann elimination was confirmed as the primary TEA decomposition route while readsorption of the decomposition products on BEA acid centers was proposed as the route that eventually leads to a residue (27). The residue, which decomposed at temperatures higher than 773 K in the presence of O_2, was thought to be composed of strong bases including NH_3 adsorbed on acidic sites. However, only 50% of the total nitrogen was accounted for in the product material balance, so the authors assumed that N_2, which could be not be quantified with the experimental apparatus, was a product of the decomposition process (27).

In this paper, we will show that the presence of O_2 during the calcination of as-synthesized BEA strongly affects the process of TEA decomposition resulting in the formation of a residue. Even low O_2 partial pressures initiate partial oxidation reactions with TEA which produce heavy residues at moderate temperatures. Unexpectedly, more residue is formed in the presence of O_2 at 750–770 K than in its absence.

EXPERIMENTAL

Four samples of BEA were synthesized from gels with the following compositions:

BEA-20	$19.8\,SiO_2 \cdot 2.00\,TEA_2O \cdot 1.80\,MTEA_2O \cdot 1.31\,Na_2O \cdot Al_2O_3 \cdot 212\,H_2O$
BEA-22	$22.1\,SiO_2 \cdot 2.00\,TEA_2O \cdot 1.80\,MTEA_2O \cdot 1.31\,Na_2O \cdot Al_2O_3 \cdot 206\,H_2O$
BEA-30	$30.0\,SiO_2 \cdot 3.75\,TEA_2O \cdot 1.50\,Na_2O \cdot Al_2O_3 \cdot 450\,H_2O$
BEA-60	$60.0\,SiO_2 \cdot 7.50\,TEA_2O \cdot 3.00\,Na_2O \cdot Al_2O_3 \cdot 900\,H_2O$.

The numerical appendage in each name denotes the nominal synthesis gel SiO_2/Al_2O_3 ratio. The recipes have been adapted from those given by Hegde *et al.* (5). Chromatographic silica gel (Fisher Chemicals) was used as a silica source for BEA-20, BEA-30, and BEA-60, while fumed silica (Sigma S-5130) was used for BEA-22. Alumina sources were $NaAlO_2$ (Fisher) for BEA-30 and BEA-60 and $Al_2O_3 \cdot 3H_2O$ (LaRoche Chemicals) for BEA-22 and BEA-20. TEA–OH was supplied as a 40% aqueous solution by RSA Chemicals. Originally, the goal of the BEA synthesis was to obtain a material with a ratio of polymorph A/B which was skewed from the ratio given by Newsam *et al.* (1). One such attempt involved the substitution of methyltriethylammonium–hydroxide (MTEA–OH) as a 36.6% aqueous solution (Eastern Chemicals) for TEA–OH as noted in some of the recipes. However, we have found no distinguishable difference between materials prepared with partial replacement of TEA–OH by MTEA–OH and those prepared with pure TEA–OH by any of the techniques we are reporting in this paper, and because the properties and molecular weights of TEA and MTEA are so similar, we will not distinguish between the two further in this paper. Crystallization was performed in stainless steel autoclaves for at least 5 days at 423 K. The solids were recovered by filtration, washed to below pH 9, dried overnight at 393 K, and equilibrated over saturated NH_4Cl aqueous solution in a desiccator.

Calcinations were performed in either a microbalance or a controlled atmosphere tubular calcining furnace. The microbalance was a Perkin–Elmer TGA-7 with a versatile gas/adsorbate supply system interfaced to a PC (29). About 15 mg of sample was placed on the Pt microbalance pan and the sample was continuously swept with a 100 cm^3/min He

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[2] The authors gratefully acknowledge the contribution of a reviewer who brought these two reports to our attention.

reagent gas stream containing 0–25% O_2 or 25% H_2. The temperature was ramped linearly at 10 K/min to an upper temperature which was usually 1073 K, but other upper temperatures were used and will be highlighted where appropriate. 1-Propanamine (1-PA) thermal analysis experiments were performed in the same microbalance and these experiments often followed calcination. 1-PA was delivered to the microbalance by bubbling a pure He purge gas though the liquid at room temperature for 5 min. During this uptake period, the sample was held at 323 K. The 1-PA supply was then bypassed, and the apparatus was purged with pure He for 10 min. Thermal analysis was accomplished by linear temperature programming from 323–823 K at 5 K/min. In some cases, the effect of 25% O_2 or 25% H_2 in He on the 1-PA desorption process was tested and compared to the calcination procedure. In these cases, the temperature was ramped from 323–1073 K at 10 K/min after adsorption of 1-PA.

The tubular calcining furnace was used to calcine a 10 g sample of BEA-22. The material was spread flat on a quartz tray at about 100 mg/cm^2 to avoid deep bed steaming. The thermal treatment atmosphere was 20% dry air in Ar (giving nominally 4% total O_2) flowing at 200 cm^3/min through a 5 cm diameter stainless steel tube. Thermal conditions were 298–393 K in 0.5 h, hold at 393 K for 1.5 h, 393–773 K in 3 h, 773–848 K in 2 h, and a final hold at 848 K for 2 h before rapid cooling to room temperature. Unexpectedly, this procedure had to be repeated 3 times to generate a sample which was devoid of carbon deposits to the eye. Intermediate samples were distinctly dark indicating remnants of a residue.

A Scintag PAD-V X-ray difractometer equipped with a Cu*Kα* radiation source operated at 1.6 KW and a Kevex Peltier-cooled solid-state detector was used to obtain diffraction data.

RESULTS

Characterization of the synthesized samples included X-ray diffraction and 1-PA adsorption. X-ray diffraction patterns (Fig. 1) were all typical of BEA and also compared favorably with a commercial sample (Valfor CP-811BL-25 manufactured by PQ Corporation). Table 1 summarizes the results of 1-PA adsorption on the calcined samples. Total capacities for 1-PA at 323 K were 16–21 wt% which compares favorably with published data for other organic molecules (1, 5). Framework Al content has been deduced from the 1-PA capacity at 598 K, and the measured values are close to those expected from the composition of the synthesis gel.

Thermogravimetric (TA) and corresponding derivative curves (dW/dt) for the calcination process in pure He and 25% O_2 in He are given in Figs. 2–5 for BEA-20, BEA-22, BEA-30, and BEA-60, respectively. A calcining experiment using 25% H_2 in He for BEA-22 is also included in Fig. 3. In these figures, we have taken the weight at 403 K to be the 100 wt% reference condition. This corresponds to the temperature at which weakly bound water desorption is complete and is a better reference condition for our purposes than the initial weight because the materials begin losing weight rapidly when placed in the dry purge gas so that the initial weight is very difficult to determine accurately.

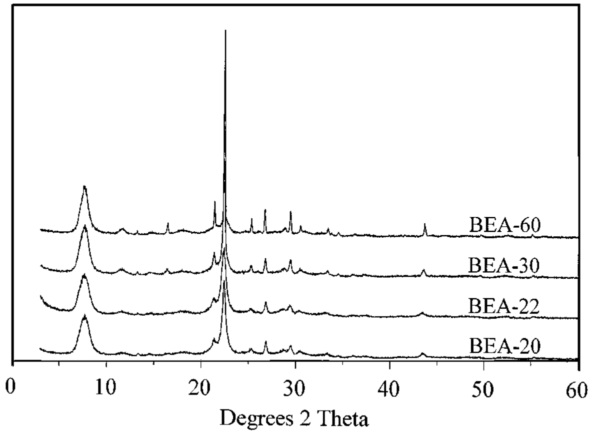

FIG. 1. X-ray diffraction patterns for BEA samples.

An examination of Figs. 2–5 quickly reveals that there is virtually no effect of the composition of the atmosphere during the calcination process in the $T < 600$ K region. The calcination processes in pure He and 25% H_2 in He atmospheres were virtually identical for BEA-22 over the entire temperature region. However, there is a clear effect related to O_2 in the calcining atmosphere in the $T > 600$ K region. In each of these figures, the TA curves for pure He and 25% O_2 in He begin to diverge near 730 K and the weight of the sample in the O_2-containing atmosphere is the higher of the two indicating the formation of a residue. The residue is relatively stable up to about 800 K and the temperature reaches 900 K before the residue has been largely burned away. A similar result can be extracted by careful examination of Figs. 10 and 11 and Table 4 in the report by

TABLE 1

Characterization of BEA Samples

Sample	SiO_2/Al_2O_3 molar ratio: Synthesis gel	SiO_2/Al_2O_3 molar ratio: Framework[a]	Al atoms per unit cell[b]	1-Propanamine adsorption, g/100 g zeolite: 323 K	1-Propanamine adsorption, g/100 g zeolite: 598 K
BEA-20	19.8	23.0	5.12	18.68	7.96
BEA-22	21.1	21.4	5.47	20.98	8.52
BEA-30	30.0	28.1	4.25	19.58	6.60
BEA-60	60.0	47.3	2.59	15.94	4.01

[a] Determined by 1-propanamine adsorption at 598 K assuming stoichiometric 1/1 1-PA/Al complexes (28).

[b] Computed assuming a BEA unit cell consisting of 64 TO_2 units.

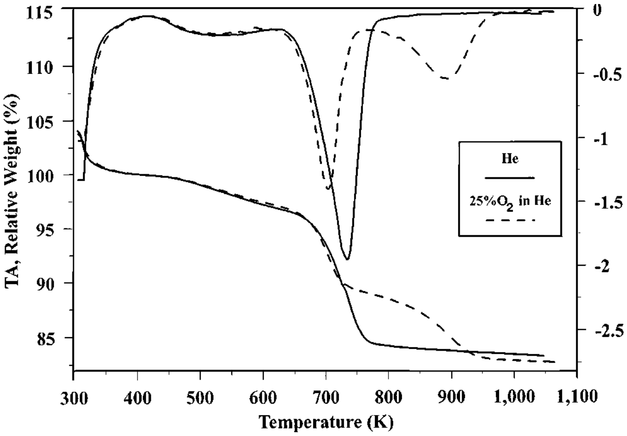

FIG. 2. Calcination of BEA-20 in He and 25% O_2 in He.

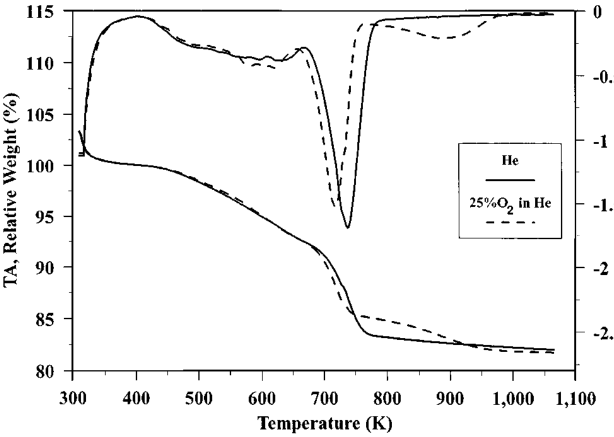

FIG. 4. Calcination of BEA-30 in He and 25% O_2 in He.

Perez-Pariente *et al.* (21) but the effect was not discussed by the authors.

In order to assess the dependence of residue formation on O_2 concentration, the BEA-22 calcining process was repeated at O_2 concentrations corresponding to 2, 4, and 10% O_2 in He. The TA curves and *dW*/*dt* spectra are compared in Figs. 6 and 7, respectively, along with the pure He and 25% O_2 in He curves previously given. As the O_2 content increases, the weight of residue increases as can be seen around 800 K in Fig. 6. However, higher O_2 contents favor the kinetics of residue removal reactions so that lower temperatures are required for complete residue removal. This observation is easily deduced by examination of Fig. 7 in the 800–1000 K region.

The essentials of the data in Figs. 2–7 are summarized and compared with further experiments in Table 2 where amounts of residue (as TEA) remaining at 450, 623, 773, and 1073 K during the calcining processes are presented. Calculations were performed by taking the weight of the samples which were heated in 25% O_2 in He as a 100 g basis at 1073 K. At 450 K (which corresponds roughly to the region where pores are completely full), BEA-20, BEA-22, and BEA-30 retain 6.1–6.4 TEA molecules per unit cell which compares favorably with literature values (12). BEA-60 retains 7.2 TEA molecules per unit cell which is slightly higher than the 6 molecules per unit cell which BEA can accommodate (12) and the excess is probably due to TEA attached to the outer surface of the crystallites. At 623 K (which corresponds to the plateau region where we expect desorption of all weakly bound material), all materials except for BEA-60 show TEA/framework-Al very near one. BEA-60 requires a higher temperature before all weakly bound material is desorbed. Also included in Table 2 is an experiment where BEA-22 was washed with 1 *N* NH_4Cl solution for 4 h prior to calcination and is termed "BEA-22, NH_4Cl washed" in the table. This process removed almost all TEA in excess of one TEA/framework-Al at 450 K and this further indicates that the TEA remaining at $T < 623$ K is indeed weakly bound. Extending the 1 *N*

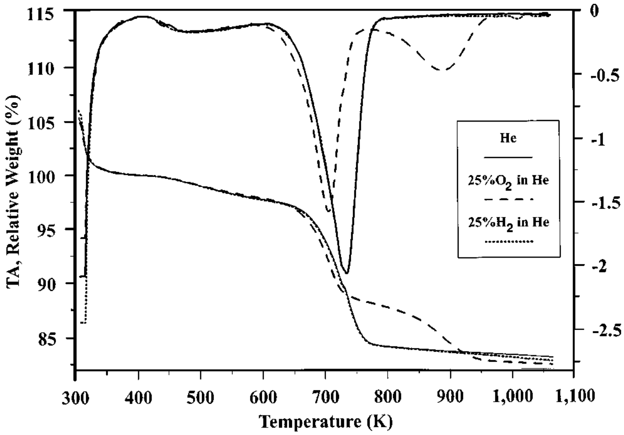

FIG. 3. Calcination of BEA-22 in He, 25% O_2 in He, and 25% H_2 in He.

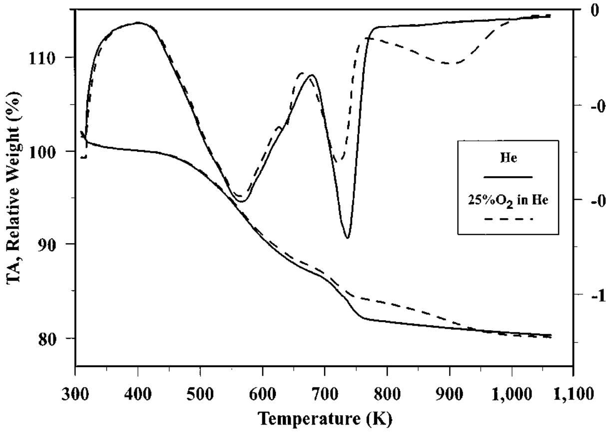

FIG. 5. Calcination of BEA-60 in He and 25% O_2 in He.

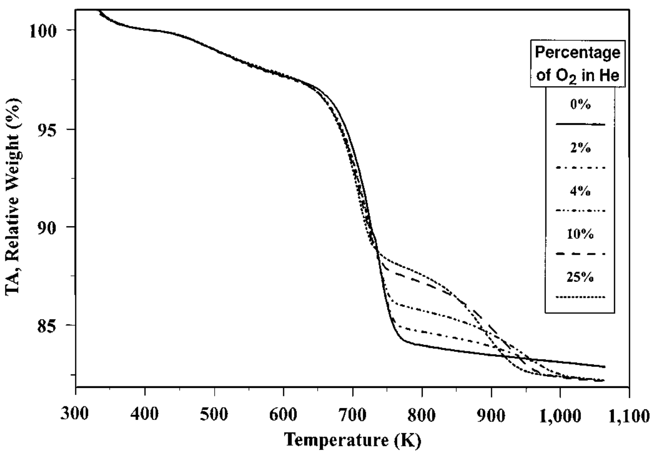

FIG. 6. Effect of O_2 content on the calcination of BEA-22.

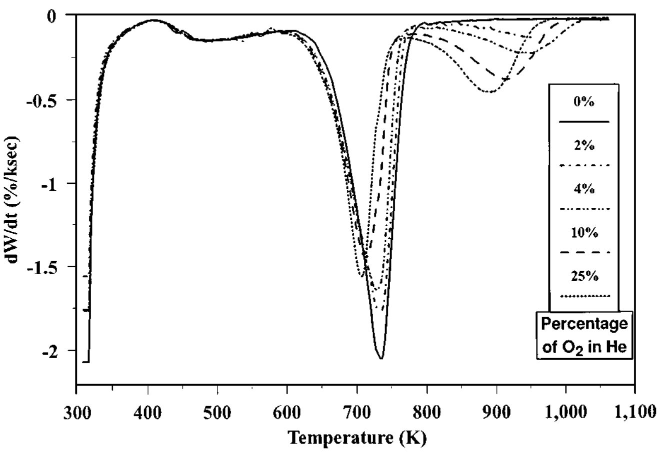

FIG. 7. Effect of O_2 content on the calcination of BEA-22.

NH_4Cl washing period to overnight had little effect on the results. At 773 K, materials calcined in pure He or 25% H_2 in He show the equivalent of 0.61–0.72 TEA molecules per unit cell but when 25% O_2 is present in the calcining atmosphere, 2–3 times the residue remains. At 10% O_2 or more on BEA-22, there is only a slight increase in residue with O_2 content. At 1073 K, no residue remains if O_2 is present in the calcining atmosphere, but a slight residue of 0.03–0.04 molecules TEA/framework-Al remains if O_2 is absent.

An immediate question which arises is whether residue formation from TEA, which can be correlated with the presence of O_2 in the calcining atmosphere, is specific to TEA or if other amines, which can be introduced by adsorption, might also form residue in the presence of O_2 during thermal treatment. We have therefore adsorbed 1-PA on BEA-22 (which had already been calcined to remove TEA) and compared thermal desorption in pure He and 25% O_2 in He. The results are given in Fig. 8 and we note a strong similarity between residue formation from 1-PA in this experiment with residue formation from TEA in experiments such as those depicted in Fig. 3. A second question is whether or not this phenomenon is specific to BEA, or if other zeolites, which may contain amine templates different from TEA, also exhibit similar behavior.

TABLE 2

Summary of BEA Template Decomposition in BEA Catalysts

		Residue at the indicated temperature (as TEA)							
	Calcining	450 K		623 K		773 K		1073 K	
Sample	atmosphere	mol/UC[a]	mol/Al	mol/UC[a]	mol/Al	mol/UC[a]	mol/Al	mol/UC[a]	mol/Al
BEA-22	He	6.22	1.14	5.42	0.99	0.72	0.13	0.24	0.04
	25% H_2 in He	6.22	1.14	5.42	0.99	0.72	0.13	0.25	0.04
	2% O_2 in He	6.22	1.14	5.39	0.99	0.93	0.17	—	—
	4% O_2 in He	6.22	1.14	5.41	0.99	1.33	0.24	—	—
	10% O_2 in He	6.22	1.14	5.40	0.99	1.87	0.34	—	—
	15% O_2 in He	6.22	1.14	5.40	0.99	1.89	0.34	—	—
	25% O_2 in He	6.23	1.14	5.43	0.99	2.03	0.37	—	—
BEA-22, NH_4Cl washed	25% O_2 in He	5.81	1.06	5.60	1.02	2.36	0.43	—	—
BEA-20	He	6.12	1.20	5.07	0.99	0.65	0.13	0.19	0.04
	25% O_2 in He	6.13	1.20	5.15	1.01	2.23	0.44	—	—
BEA-30	He	6.44	1.51	4.47	1.05	0.61	0.14	0.12	0.03
	25% O_2 in He	6.45	1.52	4.44	1.04	1.21	0.29	—	—
BEA-60	He	7.18	2.77	3.39	1.31	0.68	0.26	0.08	0.03
	25% O_2 in He	7.19	2.77	3.58	1.38	1.45	0.56	—	—

[a] UC = unit cell, see note [b] Table 1 for a definition of the unit cell.

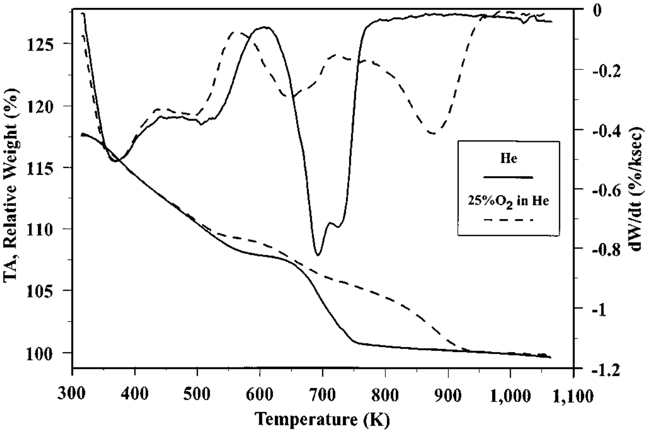

FIG. 8. Effect of O_2 on the decomposition of 1-PA in BEA-22.

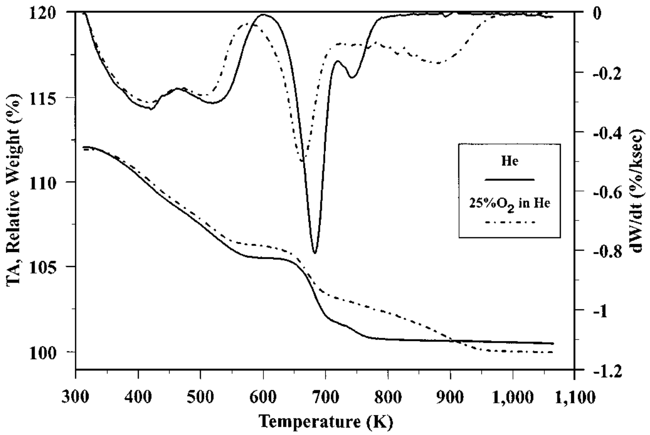

FIG. 10. Effect of O_2 on the decomposition of 1-PA in UOP–MFI.

We have therefore compared the calcining process for MFI (as synthesized material manufactured by UOP, drum 206, lot 7) in pure He and 25% O_2 in He and the results are given in Fig. 9. The primary template decomposition features at 600–800 K in the pure He case are strongly modified when O_2 is present. Some of the template decomposition can be observed at a lower temperature in the presence of O_2, but a residue which burns off at 775–925 K is also apparent. The formation of a residue from adsorbed 1-PA over MFI in the presence of O_2 can also be observed as depicted in Fig. 10. Therefore, we believe that residue formation from amines in the presence of O_2 during thermal treatment should be expected for a wide variety of zeolite/template or zeolite/amine systems.

A proper calcining treatment should yield a material which has a high adsorption capacity and acidity. We have therefore tested the materials which result from different calcining procedures with 1-PA TA and the results for BEA-22 are presented in Table 3. In all cases utilizing small microbalance samples, high adsorption capacities and acidities are determined regardless of the calcining procedure. In fact, the only sample which showed a significantly smaller acidity than the other samples was the 10 g batch treated in the calcining furnace in 4% O_2 in N_2/Ar which is sample 7 in Table 3. The adsorption capacity for this sample is comparable to the other samples, but the number of acid sites is about 30% less. This is probably due to amine residues from TEA which are strongly adsorbed on acid sites. Treatment of this sample in 25% O_2 in He at 823 K in the microbalance (sample 8, Table 3) enhances the acidity significantly.

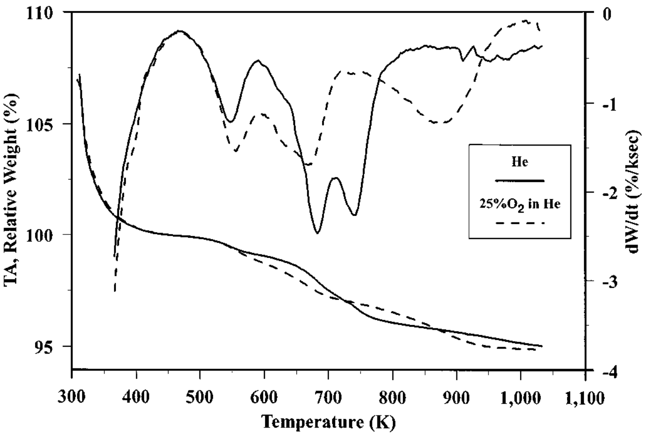

FIG. 9. Effect of O_2 on the calcination of UOP–MFI.

DISCUSSION

The utilization of an O_2-containing calcining atmosphere for the treatment of BEA which contains TEA has been widely reported (5–8, 14, 15, 19). O_2 was believed to facilitate template decomposition and to assure complete removal of all organic material from the zeolite. Therefore, the vast majority of template decomposition studies have been performed in air (5, 6, 12, 13). All the template decomposition studies report four distinct weight loss regions, and the two highest temperature features have been widely attributed to the decomposition of TEA and the degradation of amine residues. Readsorption of TEA decomposition products on strong acid sites has been assumed to precede residue formation (27) but the composition of the residue and mechanism of formation are still undetermined.

While TA studies in this paper fully confirm observations previously reported on TEA decomposition in BEA in an O_2-containing environment, we have unexpectedly noted that residue formation is strongly suppressed when O_2 is excluded from the calcining atmosphere. In fact, O_2 controls essential features of template decomposition and we believe that specific amine oxidation reactions complete with template desorption, readsorption, and decomposition during the calcining process. Hofmann elimination has been widely cited (21, 24–27) to explain the template decomposi-

TABLE 3

Effect of Thermal Treatment on the Adsorption Capacity and Acidity of BEA-22

Sample	Treatment[a]	1-Propanamine adsorbed at 323 K g/g zeolite	Acidity[b] g 1-PA/g zeolite	Acidity[b] mmol 1-PA/g zeolite
1	0.05 h, 1073 K, He	0.2097	0.0825	1.398
2	0.05 h, 1073 K, 25% O_2 in He	0.2142	0.0794	1.346
3	2 h, 848 K, He	0.2214	0.0853	1.446
4	823 K, He	0.2183	0.0848	1.437
5	0.5 h, 823 K, He + 1.5 h, 823 K, 25% O_2 in	0.2270	0.0883	1.497
6	He	0.2278	0.0880	1.492
7	2 h, 823 K, 25% O_2 in He	0.2135	0.0549	0.931
	Large sample heated at 848 K in 4% O_2 in			
8	N_2/Ar, repeated 3 times[c]	0.2143	0.0664	1.125
	Sample 7 treated in the microbalance at 823 K for 2 h in 25% O_2 in He			

[a] 10–15 mg sample in the microbalance pan heated at 10 K/min to the final temparature using 100 cm^3/min gas flow unless otherwise noted.

[b] Estimated at 598 K from the "plateau" region of the 1-PA desorption curves (29).

[c] 10 g BEA-22 was placed in a quartz tray forming about a 10 mm deep bed.

tion features, but we believe further reactions which require O_2 are also important. This hypothesis is fully supported by our comparative study of TPA decomposition in MFI with and without O_2, and 1-PA TA with and without O_2.

Recent work by Parrillo *et al.* (28) contributed greatly to our understanding of the zeolite/amine system by linking decomposition features to the stability of the adsorbed alkylammonium ions. Since the basicity of NH_3 and alkylamines increases in the sequence (30)

$$NH_3 < \text{primary} < \text{secondary} < \text{tertiary},$$

polyalkylammonium ions are expected to decompose at higher temperatures than ammonium and monoalkylammonium ions. This was recently observed in the H–MFI system where adsorbed 1-PA decomposition was observed at 670 K but adsorbed dipropylamine required a higher temperature of about 750 K. Still more generally, amine molecules are adsorbed at different strengths depending upon whether they are adsorbed directly on a proton site, or whether they participate in the formation of "solvation shells" surrounding molecules already adsorbed at proton sites (29, 31).

In the case of amine decomposition in the absence of O_2, we distinguish a sequence of three basic steps as the temperature is raised. The first step includes desorption of amine which is either occluded in channels or participating in second level solvation shells. Readsorption of these species at reactive proton sites cannot occur because strongly adsorbed species remain on reactive sites. In the second step, decomposition of alkylammonium ions occurs, probably by stepwise dealkylation, which liberates proton sites. Side reactions of the products of decomposition including oligomerization, cyclization, and hydrogen transfer can take place on the liberated acid sites leading to the formation of some residue. Finally, in the third step, decomposition and transformation of the residue takes place above 780 K. A small fraction of the organic template eventually forms a coke that is stable to 1073 K.

In the presence of O_2, a different sequence which involves O_2 is envisaged. Classical organic chemistry teaches that amines react selectively with O_2 at moderate temperatures. In general, oxidation occurs at the α-carbon of the alkyl group or oxygen can attach to the nitrogen atom in the amine group (32) and we presume that these reactions can take place in the course of zeolite calcination. We therefore propose four temperature regions for template decomposition in the presence of O_2 corresponding to the four general features which are often reported (5, 6, 12, 13). The first region covers temperatures below 600 K for TEA in BEA where there are no specific effects attributable to the presence of O_2. Adsorbed amines which reside in the channels or may be associated with second layer solvation shell desorb unreacted. In region two, ranging roughly 600–750 K, O_2 facilitates TEA decomposition in BEA and we propose that O_2 attacks at the α-carbon and promotes dealkylation. Even in the absence of a catalyst, O_2 promotes dealkylation as evidenced by a report that triethylamine oxidizes at $T > 473$ K yielding ethylamine and acetaldehyde (33). At about 740–770 K, characteristic of region three, O_2 is involved in reactions which lead to the formation of a residue by polymerization, cyclization, and condensation. Nitroxides (N_1N substituted NO radicals) (34) are feasible at these temperatures and are known to be very reactive for dimerization and disproportionation reactions which can easily lead to residue formation. As an example, oxidation of diphenylamine produced diphenyl nitroxide on alumina or N_1N-diphenylbenzidine on silica–alumina (35). At this early period of research, more studies are necessary to confirm the mechanism of residue formation. In the final stage of thermal treatment (stage four), O_2 burns off the residue. The temperature range varies with O_2 content such that lower temperatures are required with higher O_2 contents, but temperatures generally greater than about 800 K favor the combustion process.

Finally, the results of this study strongly suggest alternatives for efficient calcination of zeolites which contain organic amine templates. Almost all of the organic amine can be removed by heating in the absence of O_2 to temperatures of 750–850 K. The absence of O_2 not only minimizes the formation of residue, but also assures that thermal runaways or explosions are not favorable. This is advantageous not only from the personal safety perspective but also from the consideration of conditions which promote stability of the zeolite product. The small amount of residue which generally forms may be removed with treatment at 800–850 K in air. A relatively high O_2 content is preferable for this process to promote the kinetics of combustion, and a thermal runaway is not likely because of the low residue content. Thus, the entire process may be performed in a relatively short period of time without requiring temperatures above about 850 K. Contrast this with the use of 4% O_2 in an inert atmosphere (which we have typically used) which either requires a temperature as high as 1073 K or extended periods of time at 850 K for efficient removal of all organic material.

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