2. Synthesis of Sodium Hexamethonium Eu-1

The synthesis of zeolite Eu-1 was carried out in accordance with the procedure given in Example 6 of the ICI European patent application 0042226. Eu-1 was found to be a metastable phase under these synthesis conditions. As reaction time proceeds, the Eu-1 formed dissolves and recrystalizes as a mixture of quartz and α-cristobalite. Scanning electron micrographs of the α-cristobalite phase obtained are shown in Figure 78 e,f. Figure 79 shows the metastable crystallization curves for Eu-1 formed at three different temperatures i.e., 180 C, 200.C, and 220 C. At each temperature Eu-1 was metastable although the transformation to quartz and α-cristobalite proceeded slowly at the lowest temperature. The Arrhenious plot of the rate of nucleation and crystallization is shown in Figure 80. The apparent activation energies for nucleation and crystallization were found to be 18.92 kcals/mole and 10.94 kcals/mole, respectively. The literature XRD line patterns for quartz and α-cristabolite are given in Figures 75 and 82, respectively. The literature XRD line pattern for Eu-1 as synthesized is given in Figure 82. The crystallite size was determined by SEM to be 1-5μm. Scanning electron micrographs for 10,30 and 90 hours reaction time at 220 C are shown in Figure 73 a,b,c,d, respectively.

Figures 78 e,f. Scanning electron micrographs of the α-cristobalite phase.

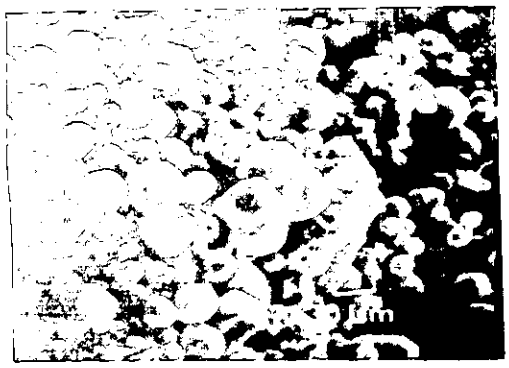


Figure 78 a

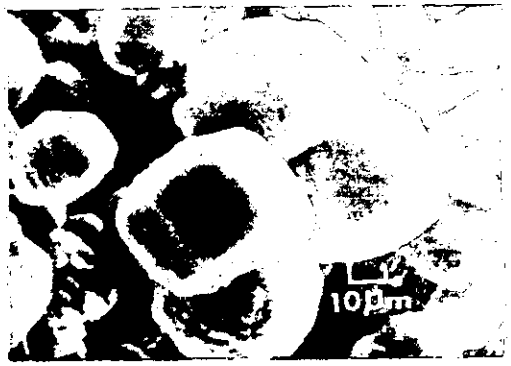


Figure 78 b

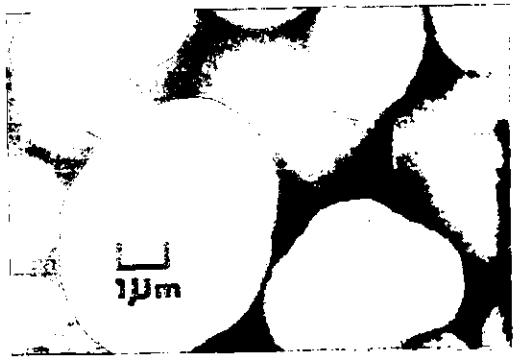


Figure 78 c

Figure 78 d

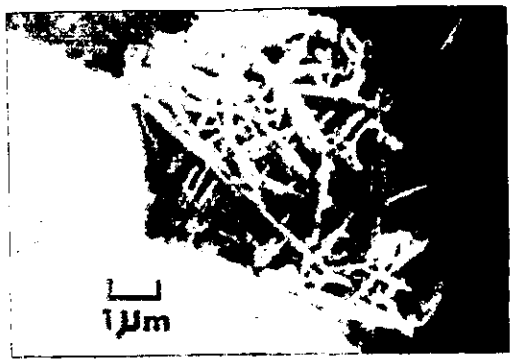


Figure 78 e

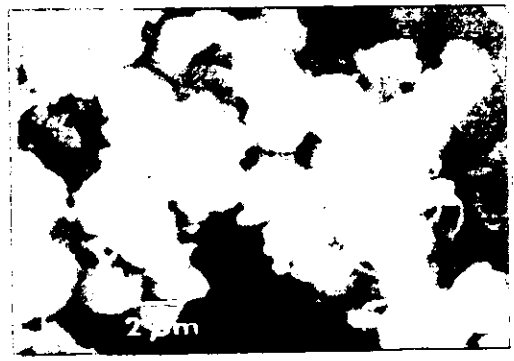


Figure 78 f

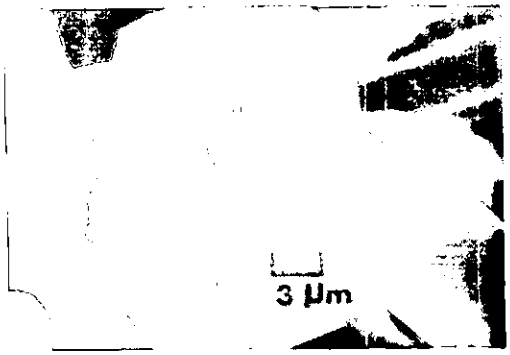


Figure 78 g

Figure 78 h

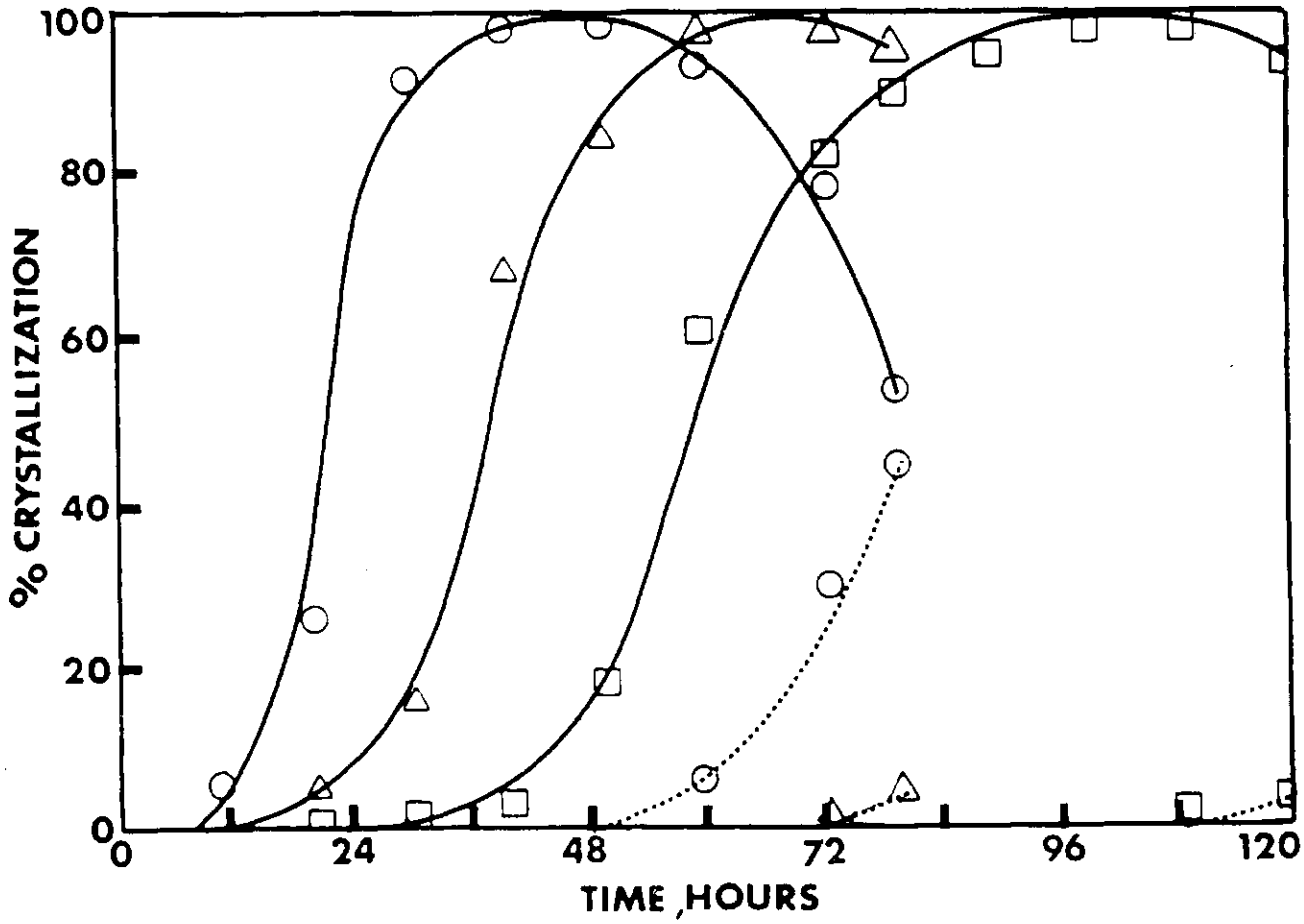


Figure 79. Rate of Crystallization in the Synthesis of Sodium Hexamethonium Eu-1.
Example 6 European Patent Application 0042226

○ - 220 C

△ - 200 C

□ - 180 C

____ Eu-1

--- Quartz + α-Cristobalite

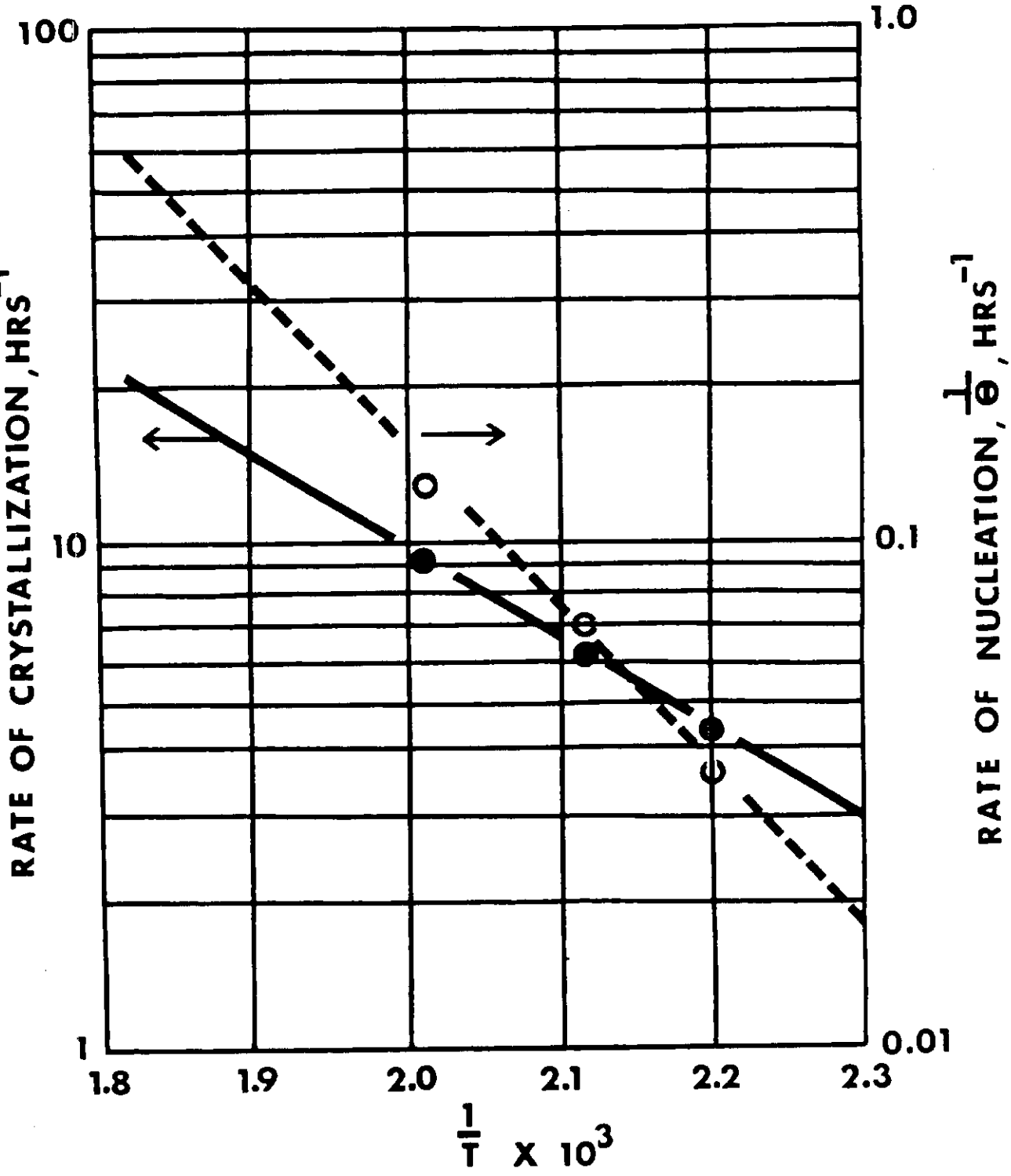


Figure 80. Arrhenious Plot of the Rate of Nucleation and Crystallization of Eu-1

Figure 81. XRD Literature Line Pattern for α-Cristobalite.

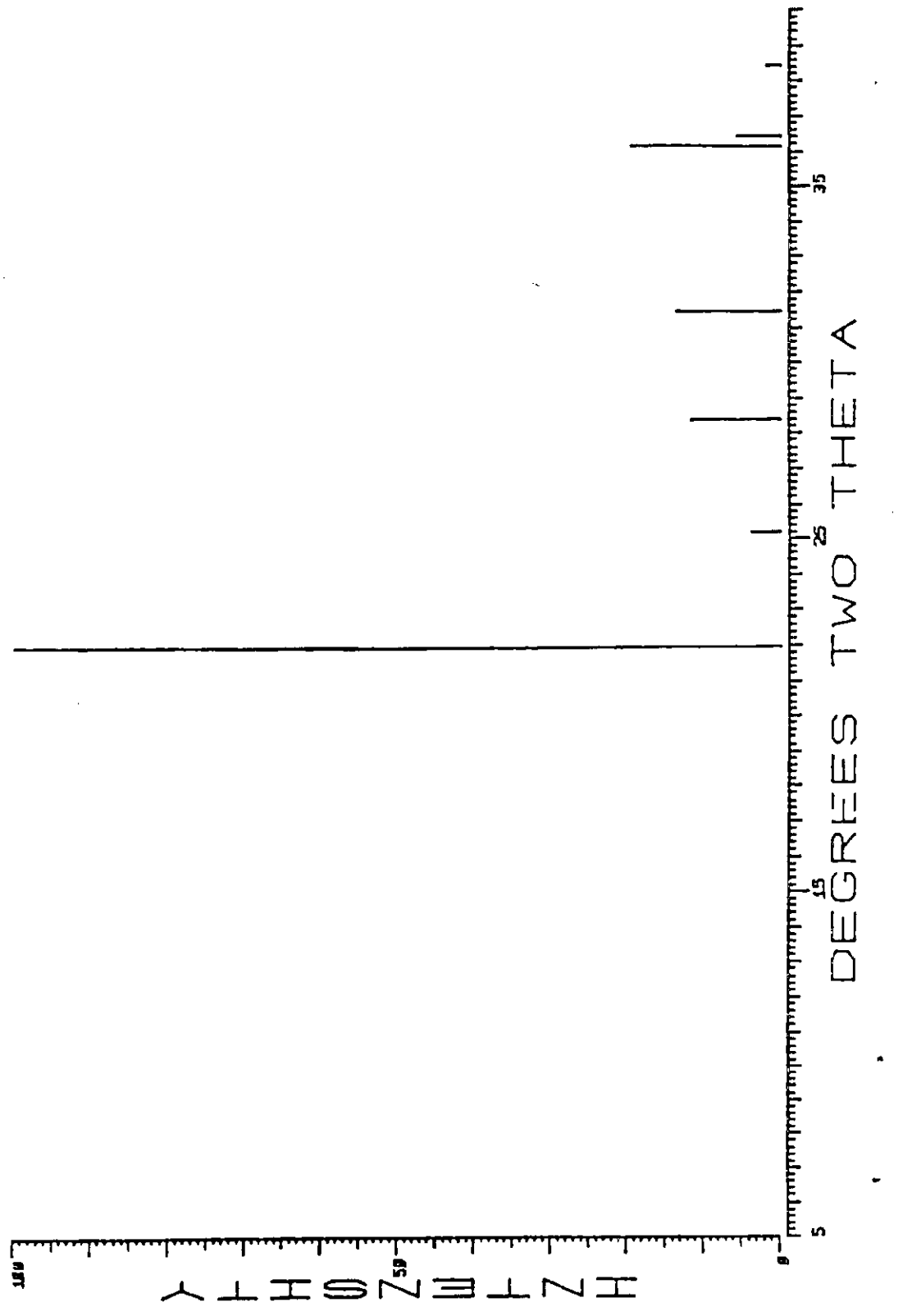
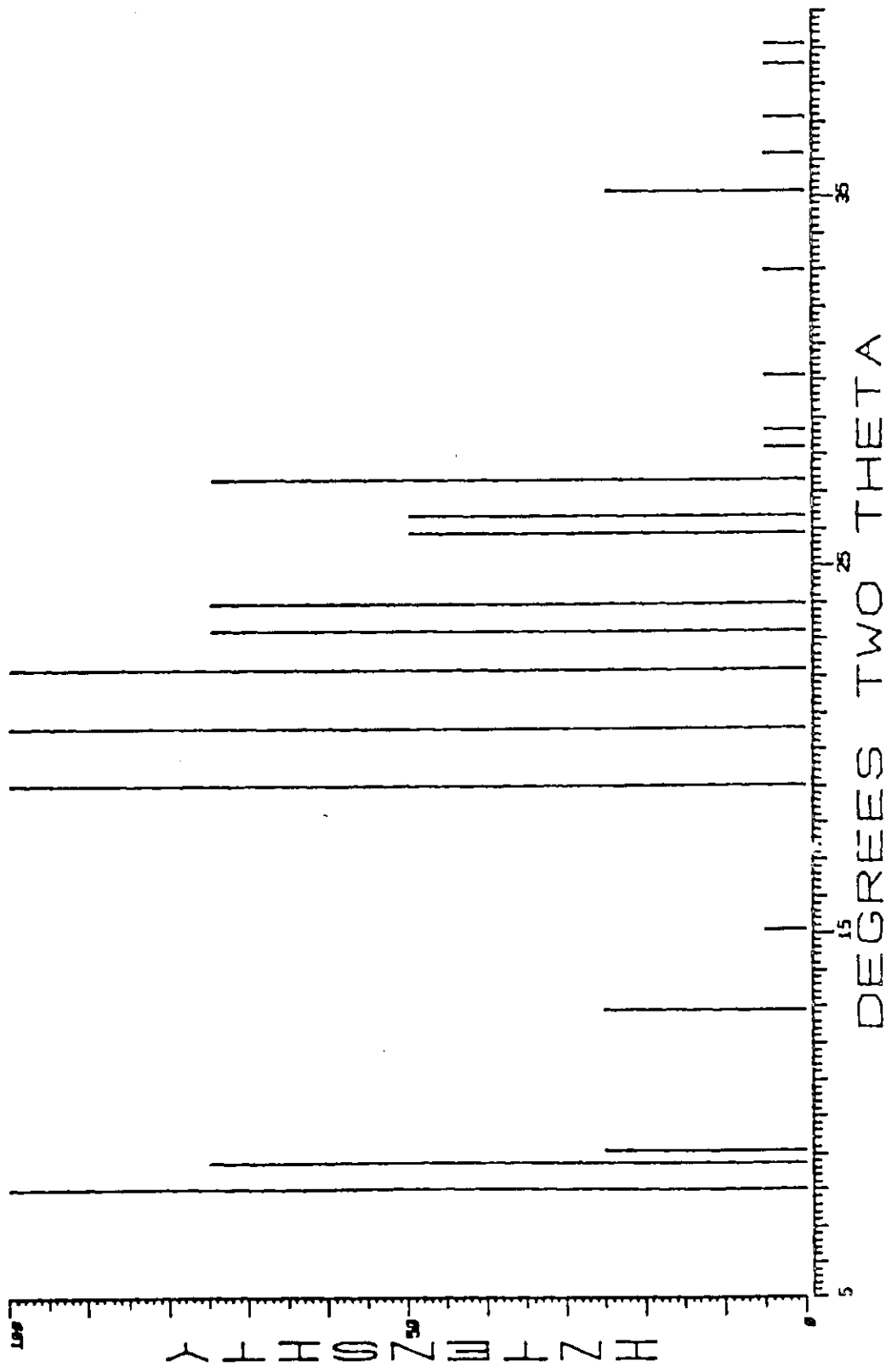


Figure 82. XRD Literature Line Pattern for EU-1 as Synthesized.



3) Effect of $\frac{(NH_4)_2O}{Na_2O + (NH_4)_2O}$ in the Synthesis of EU-1

Problems of metastability encountered in the synthesis of EU-1 were not rectified by reducing hydrothermal reaction temperature (see last section). The addition of a mineralizing agent (NH_4OH) to the synthesis batch was undertaken to stabilize the EU-1 phase. The rate of crystallization of Eu-1 as a function of $(NH_4)_2O/((NH_4)_2O + Na_2O)$ ratio was evaluated for 0.25,0.50 and 0.75. The results obtained are shown in Figure 83. The rate of nucleation and crystallization were lowered and the EU-1 formed was stable and extremely well crystallized. The crystallite size increased over ten fold. Single soap-bar shaped crystals 30μm and over were observed by SEM. The scanning electron micrographs shown in Figure 84 g and h show the morphology of the EU-1 crystals formed when $(NH_4/_2O/(NH_4)_2O + Na_2O = 0.25$. The scanning electron micrographs shown in Figure 84 a,b,c,d,f depict the typical morphologies of the larger crystals formed when $(NH_4/_2O/(NH_4)_2\ O + Na_2O) = .50$. The x-ray diffraction pattern of this high purity EU-1 product is shown in Figure 85.

Effect of Stirring in the Synthesis of EU-1 where

$$\frac{(NH_4)_2O}{Na_2O + (NH_4)_2O} = 0.25$$

The crystals formed in the synthesis of EU-1 at 200 C wherein the $(NH_4)_2O/(Na_2O + (NH_4)_2O) = 0.25$ were well formed and contained no co-existing phases as evidenced by SEM and XRD. Their size, however, approximately 30μm was undesirably large for catalytic purposes and likely to invoke diffusional limitations on the STG reaction rate. It was desired, therefore, to maintain the high purity of the EU-1 synthesized but reduce its crystallite size. Toward this end procedures found effective in reducing the crystallite size of other zeolites, notably ZSM-5, were applied to the synthesis of EU-1. The synthesis reaction was carried out in a stirred pan autoclave for 24 hours at 150 C following which the temperature was increased to 200 C for 48 hours. The product was 100% EU-1 and the crystal size was submicron.

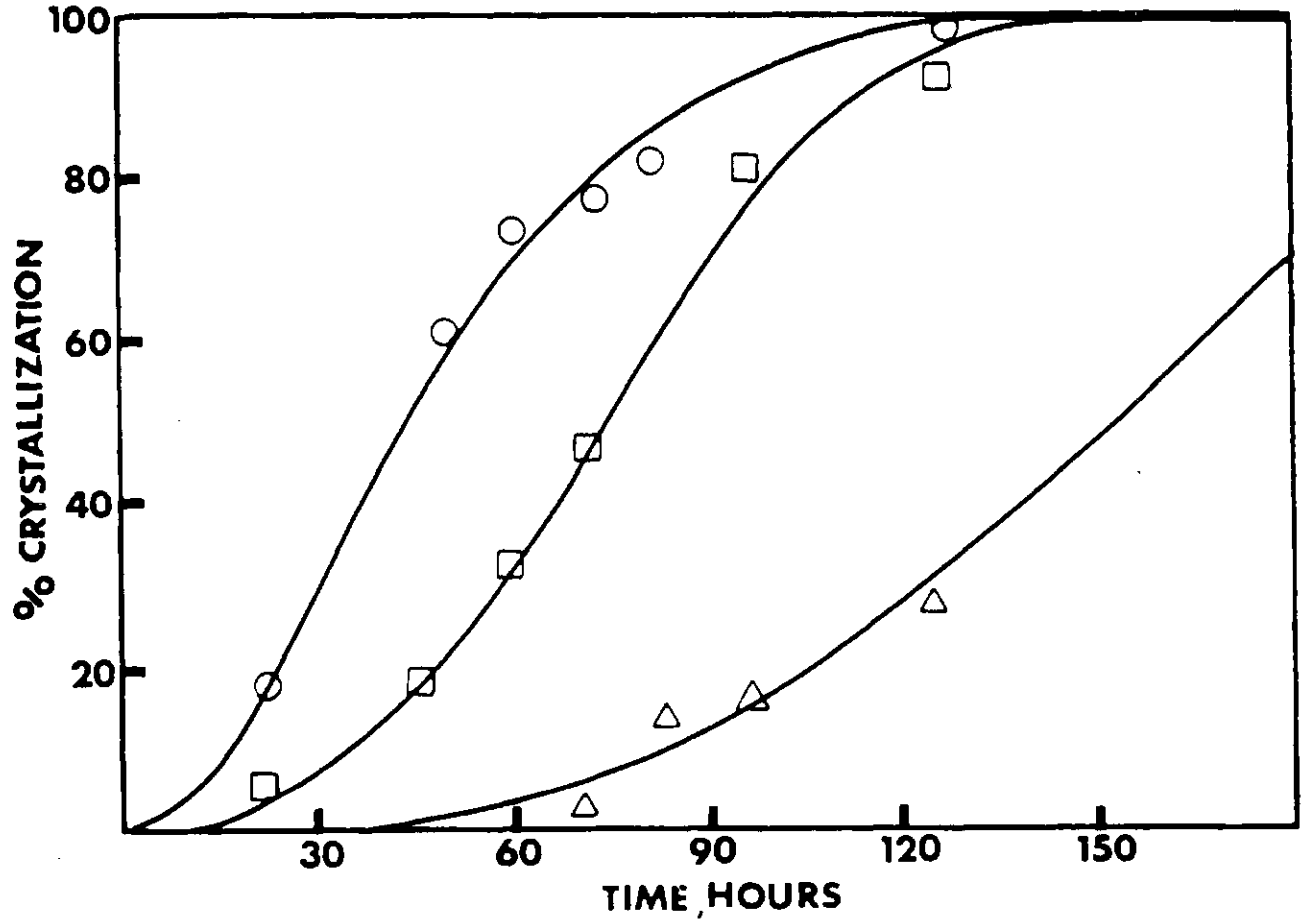


Figure 83. Crystallization Rate of EU-1 as a function of $\frac{(NH_4)_2O}{Na_2O \cdot (NH_4)_2O}$ at 200 C

○ - 7.5 Na_2O · 2.5 $(NH_4)_2O$ · 10 hexamethonium bromide - Al_2O_3 · 60 SiO_2 · 3000 H_2O

□ - 5.0 Na_2O · 5.0 $(NH_4)_2O$ · 10 hexamethonium bromide · Al_2O_3 · 60 SiO_2 · 3000 H_2O

△ - 2.5 Na_2O · 7.5 $(NH_4)_2O$ · 10 hexamethonium bromide · Al_2O_3 · 60 SiO_2 · 3000 H_2O

$$\frac{(NH_4)_2O}{Na_2O \cdot (NH_4)_2O} \quad \begin{matrix} = 0.25 & - \text{ O} \\ = 0.50 & - \\ = 0.75 & - \end{matrix}$$

Figure 84,g,h. Morphology of EU-1 Crystals Formed.

a,b,c,d,f. Typical Morphologies of the Larger Crystals Formed

Figure 84 a.

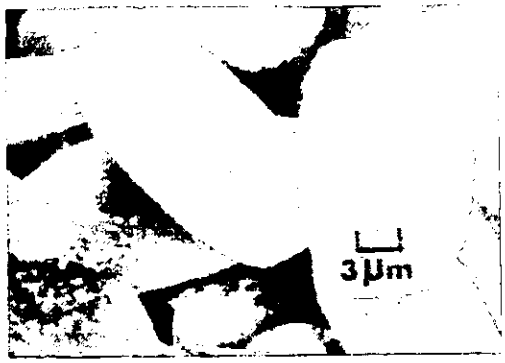


Figure 84 b.

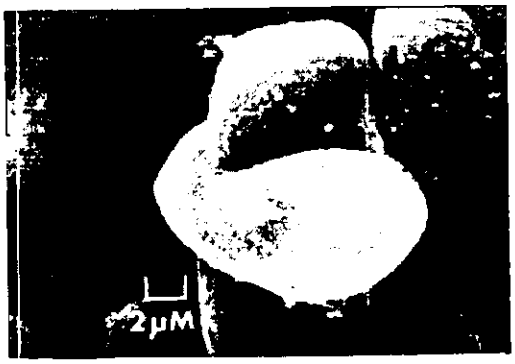


Figure 84 c.

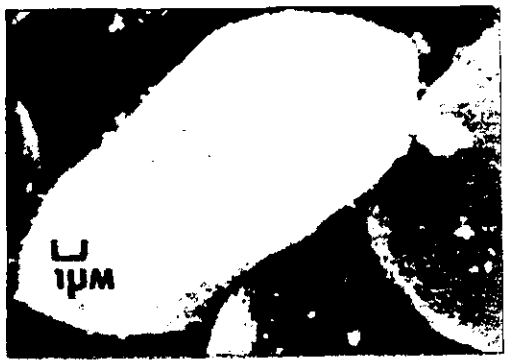


Figure 84 d.

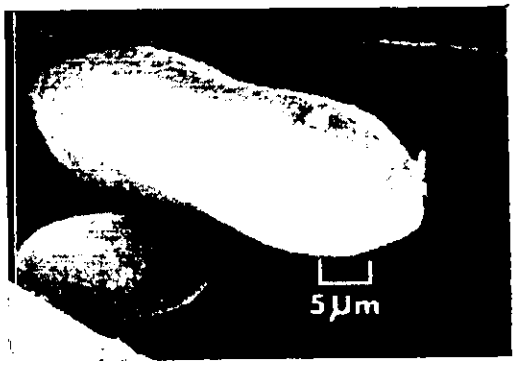


Figure 84 e.

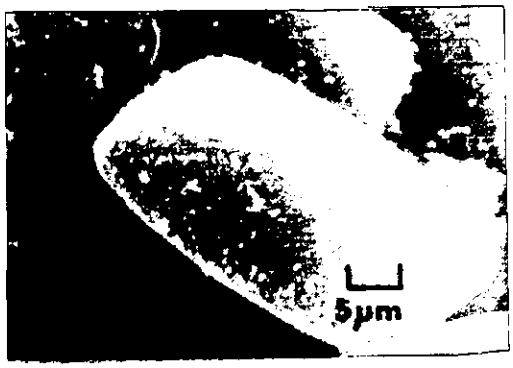


Figure 84 f.

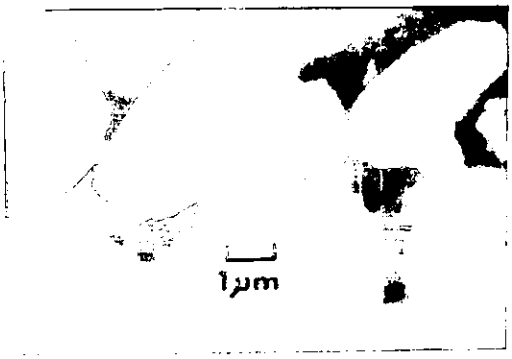


Figure 84 g.

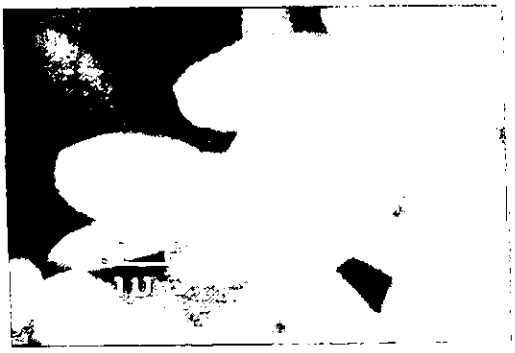
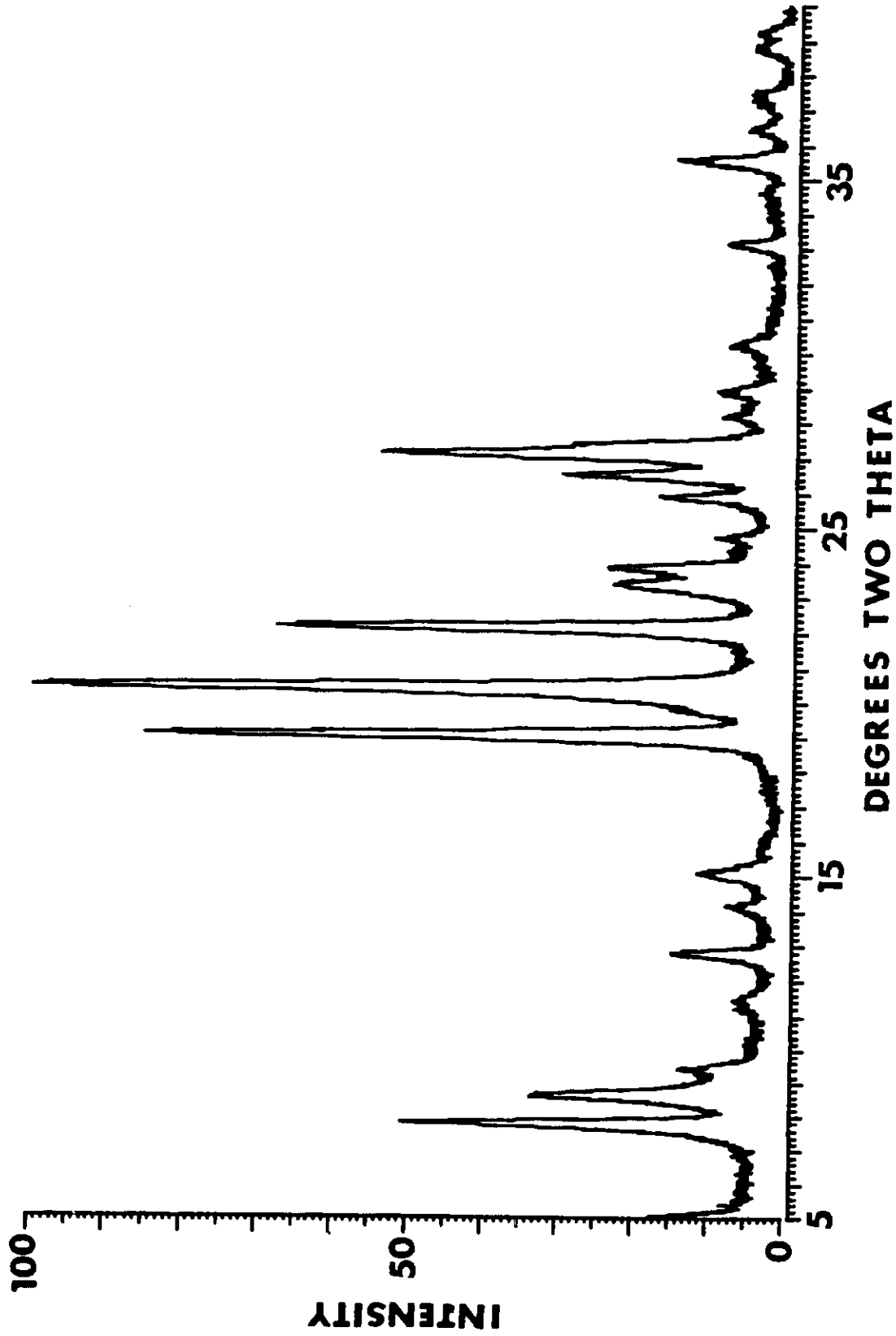


Figure 84 h.

Figure 85. XRD Pattern For EU-1



4) First Synthesis of EU-1 in a Na-Free System

If zeolite EU-1 is formed in a system containing Na it must first be calcined to remove occluded hexamethonium bromide cations by oxidative degradation and then be ion-exchanged to produce the catalytically active hydrogen form. It is desirable to produce zeolite EU-1 in a system not containing Na ion, for the ion-exchange step could then be avoided for EU-1 would be in its hydrogen form following calcination. Sodium free zeolite EU-1 was synthesized in the system $2.5(NH_4)_2O$ · 10 hexamethonium hydroxide · $1Al_2O_3$ · 60 SiO_2 · 3000 H_2O. The hexamethonium hydroxide was prepared from hexamethonium bromide by reaction with silver oxide to form hexamethonium hydroxide and silver bromide which precipitates. X-ray diffraction analysis showed good crystallinity. The pattern being similar to Figure 85. Scanning electron micrographs 86 a,b,c show the typical crystal morphologies obtained in the sodium free system. In attempt to produce a bifunctional iron-EU-1 catalyst by direct synthesis 2 wt.% iron as ferric hydroxide were added to the aforementioned batch composition. Iron was found not to impede the crystallization of EU-1. Although, the crystals formed changed to a cauliflower morphology shown in Figure 86, f,g,h. Diffraction analysis showed good crystallinity.

Figure 86 a,b,c Typical Crystal Morphologies Obtained in Na-Free System. f,g,h 2wt.% Iron as Ferric Hydroxide added Crystals changed to cauliflower morphology.

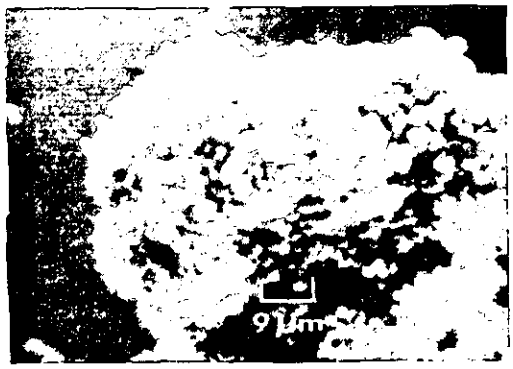


Figure 86 a

Figure 86 b

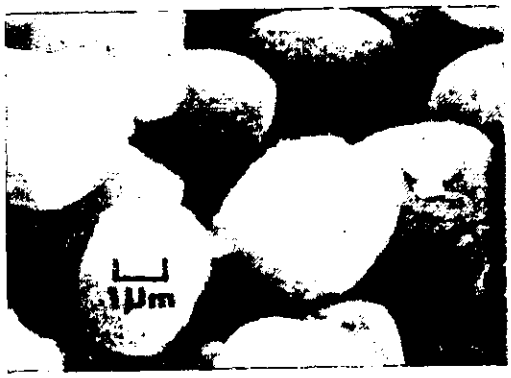


Figure 86 c

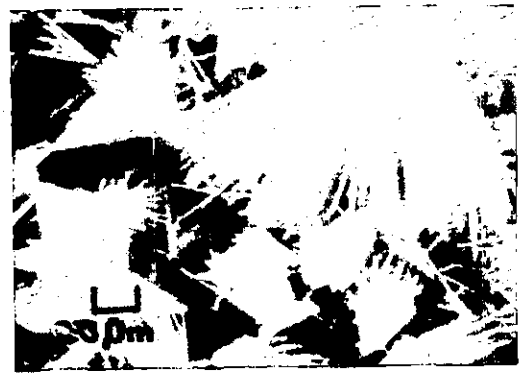


Figure 86 d

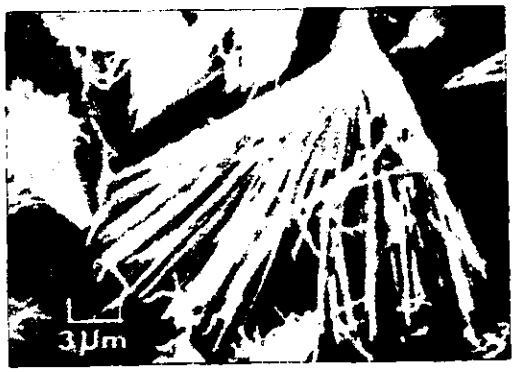


Figure 86 e

Figure 86 f

Figure 86 g

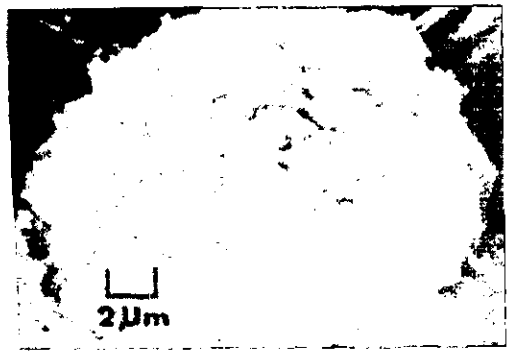


Figure 86 h

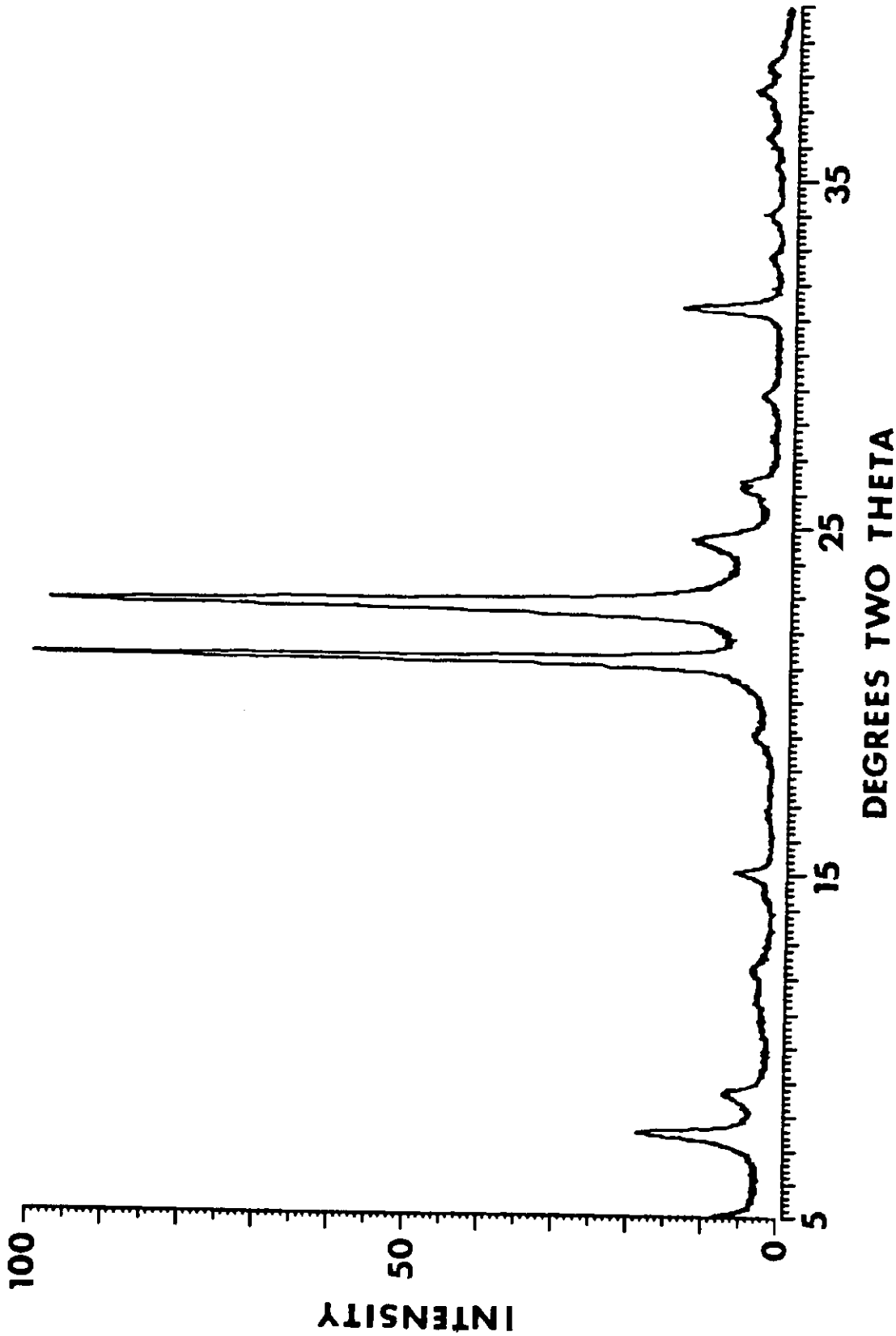
5) The Synthesis of EU-2

Zeolite EU-2 was synthesized from the same synthesis batch composition found effective in the synthesis of EU-1 excluding Al_2O_3. EU-2 is not the high silica end member of EU-1 but is an entirely different structure. The XRD pattern for EU-2 is shown in Figure 87. It is apparently equivalent to Mobil's ZSM-48 described under a U.S. patent 4,397,827. The crystallization rate curves for EU-2 grown from batch compositions 7.5 Na_2O · 25 $(NH_4)_2O$ · 10 hexamethonium bromide . 60 SiO_2 · 3000 H_2O and 5.0 Na_2O · 5.0 $(NH_4)_2O$ · 10 hexamethonium bromide ·60 SiO_2 · 3000 H_2O are shown in Figure 88. EU-2 was found to crystallize in considerable less time than EU-1. The crystals of EU-2 generally formed as radial aggregates 30 to 40 μm in diameter. Representative crystal morphologies of EU-2 grown in the system where $(NH_4)_2O/(Na_2O + (NH_4)_2O)$ = 0.50 are shown in Figure 89 a,b,c,d,e,f..

The micrograph shown in Figures 89 g,h show the typical morphology of zeolite EU-2 formed with the same batch compostion in teflon autoclaves. The previous crystals a through f were grown in steel lined autoclaves. Zeolite EU-2 can also be grown in a Na free system having a batch composition:

$2.5(NH_4)_2O$ · 10 hexamethonium hydroxide · 60 SiO_2 · 3000 H_2O. The crystals formed in the sodium free system are fibrous radial aggregates approximately 10 microns in length shown in Figure 86 d,e. Both EU-1 and EU-2 are believed to contain 10-membered ring pore systems. Their structures have not been reported. The literature XRD line pattern for EU-2 is given in Figure 90.

Figure 87. XRD Pattern of EU-2



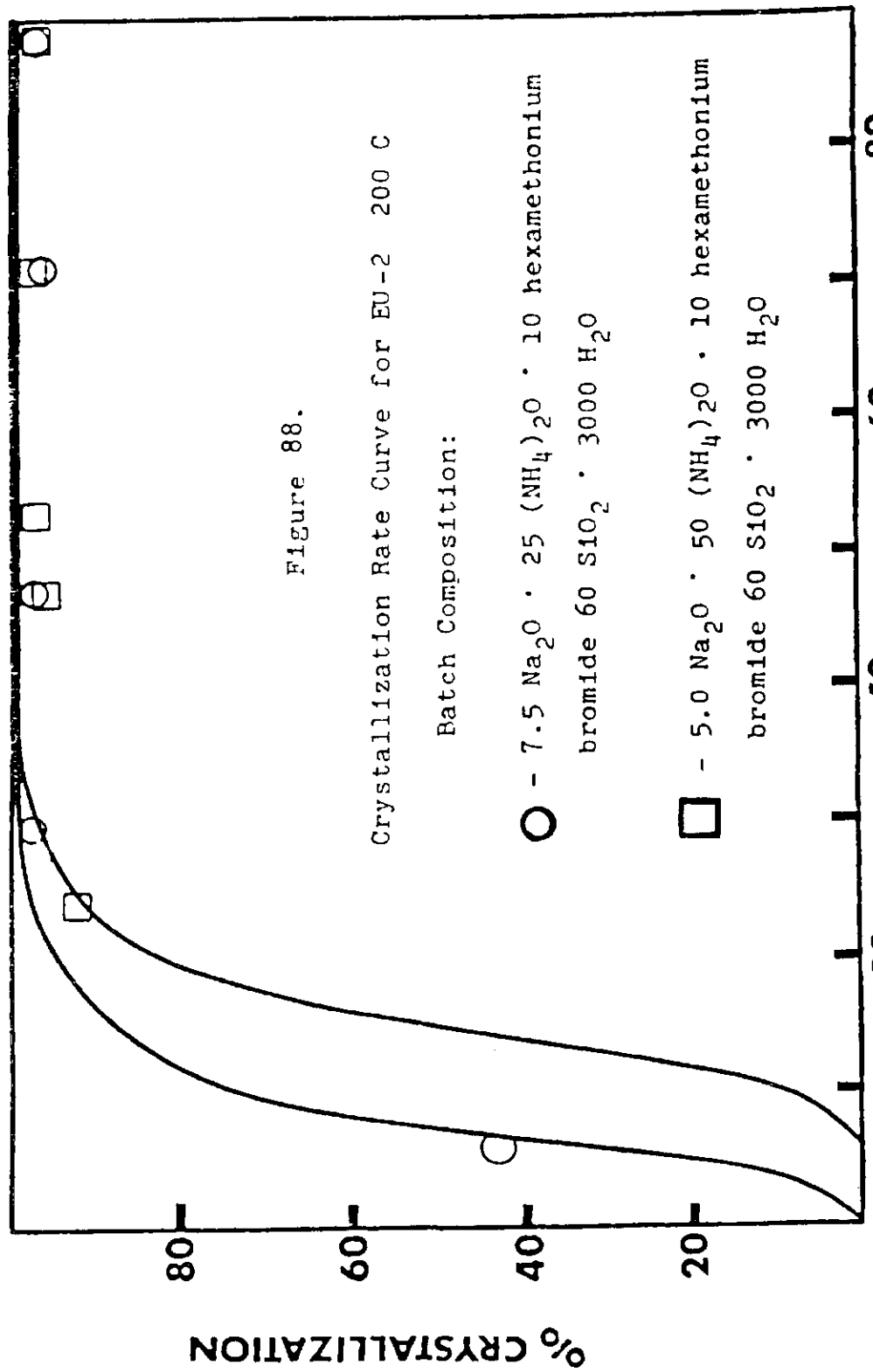

% CRYSTALLIZATION
20
40
60
80
TIME, HOURS
20
40
60
80
Figure 88.
Crystallization Rate Curve for EU-2 200 C
Batch Composition:
O - 7.5 Na_2O · 25 $(NH_4)_2O$ · 10 hexamethonium bromide 60 SiO_2 · 3000 H_2O
□ - 5.0 Na_2O · 50 $(NH_4)_2O$ · 10 hexamethonium bromide 60 SiO_2 · 3000 H_2O

Figure 89 a,b,c,d,e,f. Crystal Morphologies of EU-2 grown in the system where $(NH_4)_2O/(Na_2O+NH_4)_2O) = 0.50$.

Figure 89 a

Figure 89 b

Figure 89 c

Figure 89 d

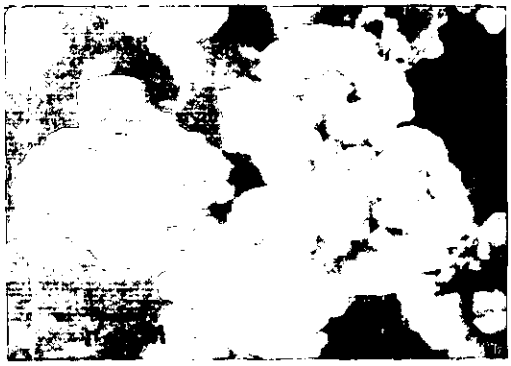


Figure 89 e

Figure 89 f

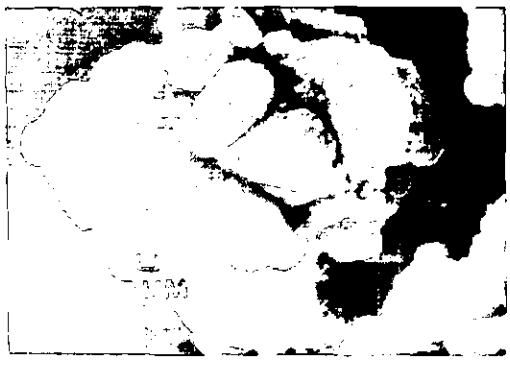


Figure 89 g

Figure 89 h

Figure 90. Literature Line Pattern For EU-2