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THERMAL ANALYSIS OF HIGH SURFACE AREA ALUMINOPHOSPHATES

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Aluminophosphates, like alumina itself, are useful as catalysts and catalyst supports /1,2/. For these applications both surface area and pore size distribution are important properties. To obtain these properties the materials are generally precipitated or crystallized from gels, using templating agents to maintain an open structure. Subsequently the templating agents can be either removed by pyrolysis or hydrolytically replaced by water (or sometimes ammonia) which is then removed by calcination. In each case high surface area solids can be obtained. Surface area and pore size are determined by the nature of the templating agents and the calcination process. The Al/P ratios are equal or larger than 1 and vary with the method of preparation. Thermal analysis has become an invaluable tool to study both composition and method.

In our laboratory we have discovered a method to produce an alumina-like aluminophosphate with exceptionally large surface area, small pores and narrow pore size distribution.

Table 1 compares two characteristic methods with ours. Thermogravimetric analysis of the product from the first method is represented by figure 1. It shows a single broad weight loss region between 50 and 100 °C, attributed to loss of organic species. Note the flat baseline following this reaction.

The wet gel obtained by the second method produced the curve shown in figure 2. The first weight loss is due to evaporation of butanol formed by hydrolysis of $Al(OR)_3$. The second weight loss is attributed to removal of triethylphosphate. In contrast to figure 1, here the baseline does not flatten out until about 600 ° due to continuing pyrolysis of bound ester groups.

For our gel, produced by the third method, the decomposition is even more complicated (figure 3). Vaporization of free butoxyethanol is followed by 2 separate weight loss regions caused by decomposition of first the mono- and then the di-ester of an organo-alumino phosphate. After hydrolysis, the two decomposition reactions are even more apparent (figure 4).

Table 2 shows the surface areas and pore size distributions of the calcination products from the three methods. The data clearly confirm the results from thermal analysis: Starting with mixtures, ill-definec gels or loosely coordinated templates, surface areas as well as pore sizes are variable. On the other hand - as with our own preparation - starting with essentially stoichiometric and strongly coordinated systems, surface areas are consistent and pores are well defined with narrow distribution.

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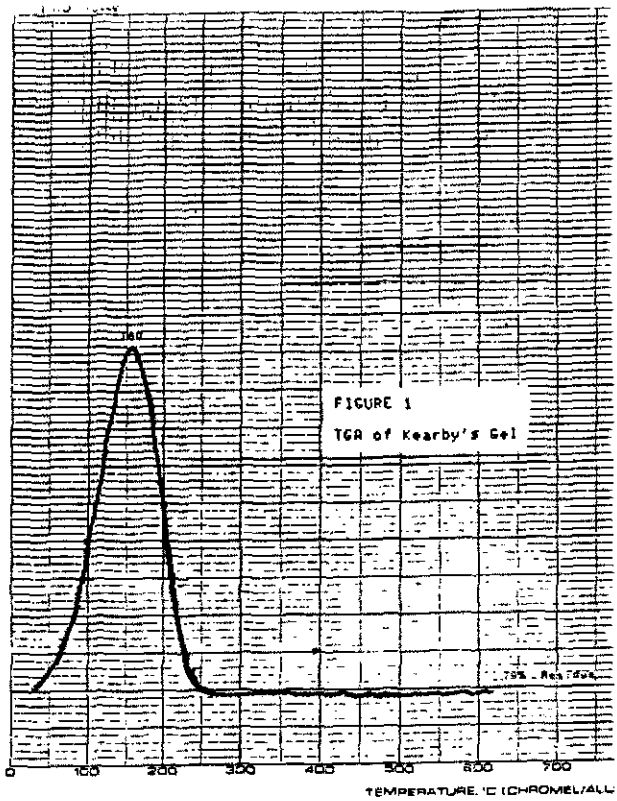
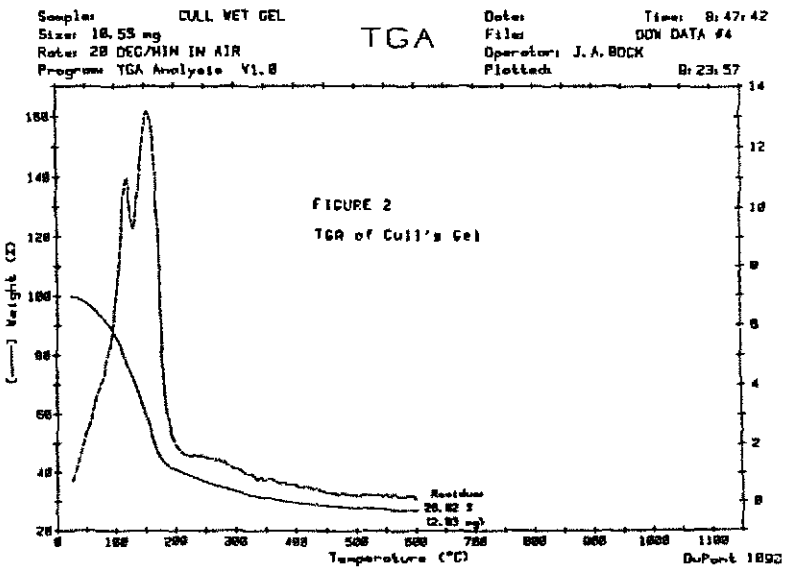


FIGURE 1
TGA of Kearby's Gel
0
100
200
300
400
500
600
700
TEMPERATURE °C (CHROMEL/ALU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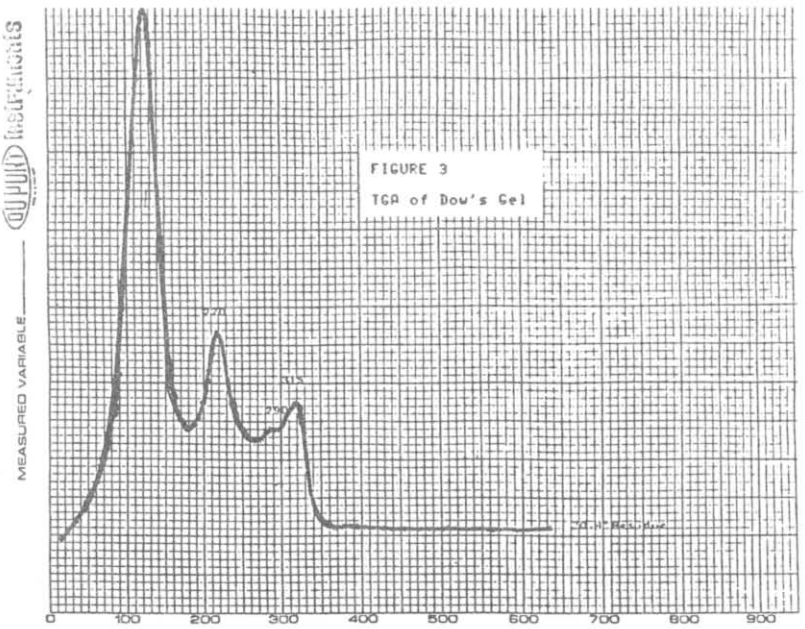
Size: 16.53 mg
Rate: 20 DEG/MIN IN AIR
Program: TGA Analysis V1.0
TGA
Date:
Time: 8:47:42
File: DON DATA #4
Operator: J.A.BOCK
Plotted: 8:23:57
FIGURE 2
TGA of Cull's Gel
(——) Weight (%)
Temperature (°C)
DuPont 1090


MEASURED VARIABLE
FIGURE 3
TGA of Dow's Gel
0
100
200
300
400
500
600
700
800
900

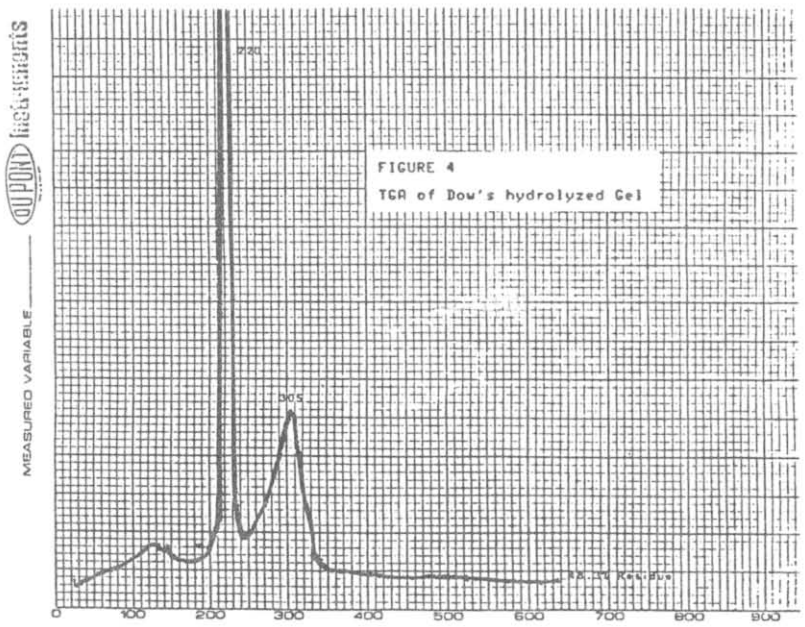

MEASURED VARIABLE
FIGURE 4
TGA of Dow's hydrolyzed Gel
0
100
200
300
400
500
600
700
800
900

Table 1

1. Kearby /3/: $H_3PO_4 + AlCl_3 + 3H_4C_2O \xrightarrow{H_2O} AlPO_4 + 3Cl(CH_2)_2OH$

2. Cull /4/: $Al(OR)_3 + OP(OR')_3 \xrightarrow{H_2O, Air} GEL \xrightarrow[N_2 Air]{1000\ F} AlPO_4$

$R = -C_4H_9 \qquad R' = -C_2H_5$

3. Dow /5/: $Al(OR)_3 + (OR)(OH)(OP)_2O \longrightarrow GEL \xrightarrow[NH_3]{H_2O} 3Al_2O_3.AlPO_4$

$R = -(CH_2)_2O(CH_2)_3CH_3$

Table 2

Method	Surface area m^2/g	Pore size A
1. Kearby	200 – 600	60 – 120
2. Cull	400 – 600	100 – 1000
3. Dow	400 – 600	50

REFERENCES

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5 Fellman, J. D., and Langer, H. G., Patent pending.