

PHASE-TRANSFORMATION OF ALUMINA TO ALPHA-ALUMINA AS AN INDUSTRIAL CATALYST SUPPORT

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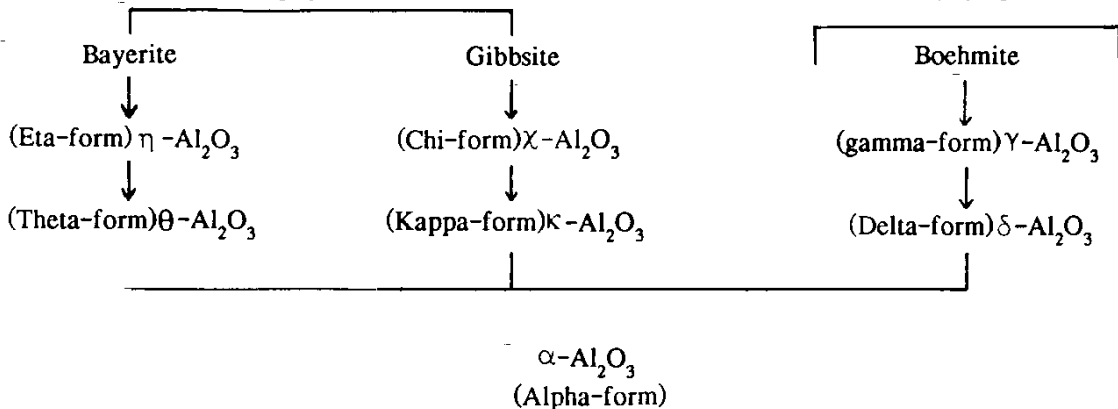
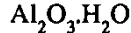
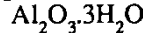
Abstract The phase transformation of aluminium hydrates yields various forms of alumina (δ , θ , κ) and eventually alpha-alumina. The decrease in the specific surface area of alumina upon heat treatment is due to changes in crystalline structure and hence a decrease in the porosity of the material. Although the conversion of gamma-alumina to alpha-structure takes place with a lowering in surface area and pores, the use of such a material as a catalyst support yields high selectivity where the acidity is lowered and the surface area is maintained to some extent sufficiently low in catalyst preparation. The yield of alpha-alumina formation on the surface of starting material (gamma alumina) was investigated by the application of the final product in catalytic dehydration of methanol to dimethyl ether via kinetics measurements. The study of phase-transition kinetics and the influence of the effective factors leads to the possibility of selecting the desired process conditions for production of high selectivity alumina support. The activity, mechanical strength and stability of the catalyst supports are desired for application in certain chemical processes. While the low specific surface area alumina is produced, the porosity may be maintained high under firing conditions: the favorable characteristics for appropriate industrial catalyst supports. The improvement of activity and selectivity of such supports is the main point of consideration.

چکیده تبدیل فازی هیدراتهای آلومینوم منجر به تشکیل انواع آلومینا (دلتا-تا-کاپا) و در نهایت نوع آلفا میگردد. کاهش سطح ویژه آلومینا در اثر حرارت مربوط به تغییرات ساختمان بلورین و در نتیجه کاهش تخلخل آن میباشد. با وجودیکه تبدیل آلومینای گاما به آلفا با کاهش سطح ویژه و تخلخل همراه است کاربرد فرآورده مزبور بعنوان پایه کاتالیستی با درجه انتخاب بالا صورت میگیرد زیرا درجه اسیدی پائین بوده و سطح ویژه تا حد لازم پائین نگاهداشته میشود تا جهت تهیه کاتالیست مناسب باشد. برای اندازه گیری میزان آلومینای آلفا که بر روی سطح ماده اولیه تشکیل میگردد فرآورده تولیدی را در واکنش کاتالیستی بی آب کردن متانول بکار برده و از اطلاعات سینتیک فرآیند مزبور استفاده شده است. مطالعه سینتیک تبدیل فازی هیدراتهای آلومینوم به آلومینای آلفا و همچنین تأثیر فاکتورهای مؤثر در تبدیل فازی مزبور امکان انتخاب شرایط مناسب برای تهیه پایه کاتالیستی آلومینا را میسر میسازد. خواص مطلوب پایه های کاتالیستی کاربردی در فرآیندهای شیمیایی عبارتند از فعالیت شیمیایی، مقاومت مکانیکی و پایداری آنها که با انتخاب شرایط حرارتی مناسب در تبدیل فازی آلومینا ممکن است ماده تولیدی دارای سطح ویژه پائین و تخلخل بالا باشد که برای تهیه کاتالیست های صنعتی مناسب است. بالا بردن فعالیت شیمیایی و درجه انتخاب پایه های کاتالیستی جهت کاربردهای مختلف مورد توجه است.

INTRODUCTION

Production of alpha-alumina is performed by either calcination of the aluminium hydroxides, the phase transition of aluminas and aluminium salts or by solidification of melts[1]. The calcination method is widely used in industrial production of alpha-alumina at temperatures below the sintering level. Phase transformation

of gamma-alumina to the alpha-form involves heating at 1100-1200°C. This temperature range may be altered by some variations in heating conditions as well as the influence of foreign gases and additives. The particle size of starting materials, the impurity and the porosity and surface area which determine the activity, are important parameters in the characteristics of the



final products.

The aluminium hydrate $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Al}(\text{OH})_3$ consists of Bayerite and Gibbsite compounds, while $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{Al}(\text{OH})$ consists of several phases from which Boehmite is of interest. The compound $\text{AlO}(\text{OH})$ yields $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ by heating where the number of crystalline water becomes lower with the extent of heating.

The eta, gamma and alpha forms are applied as catalyst supports in various hydrocarbon catalytic processes. The eta and gamma forms show both Brønsted and Lewis acidity, the theta and delta forms exhibit Lewis acidity, while alpha alumina catalysts are of hexagonal close packing with low surface area. The alpha form may be prepared in a wide range of specifications such as crystalline dimension, surface area and purity. The crystal dimension ranges from 0.03×10^{-3} mm to 30mm and the crystal shape is either needle or thin plates depending on the extent of firing. Phase transformation takes place at temperatures just below the sintering level [2].

The factors influencing alumina phase transitions are temperature, the extent of disorder, the particle size of starting material, the presence of gases in the calcination atmosphere, the impurities of the initial material and the promoting and retarding additives which affect the crystal growth as well as the other properties. The nature of the heating atmosphere affects the rate of sintering and thus the residual porosity in the final product [3-5].

EXPERIMENTAL

Phase transformation of gamma-alumina was performed at temperature range 750-1200°C, in the presence of pure nitrogen gas, pure hot steam, nitrogen and steam mixture, pure oxygen and air. A tubular induction furnace with a

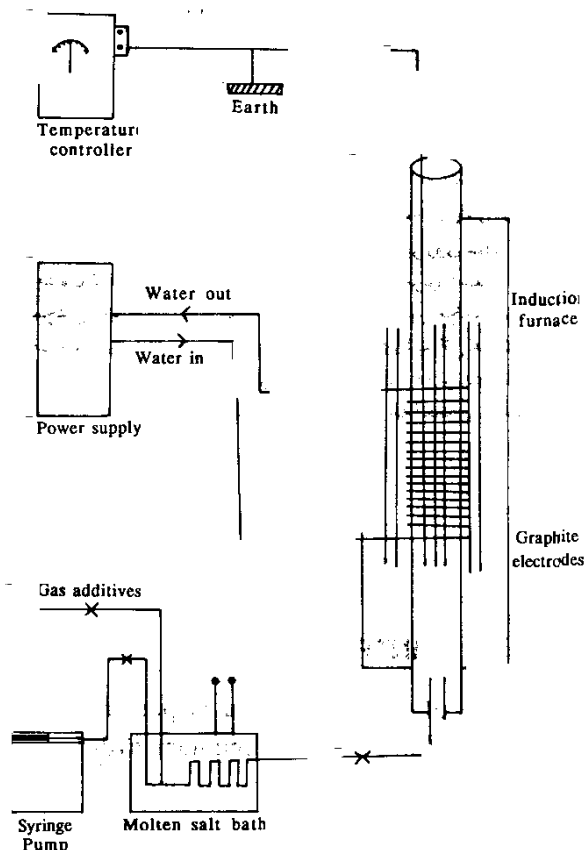


Figure 1. Schematic heating system for phase-transformation of alumina

thermostatically temperature controller was used where the precision of the temperature was monitored through a thermocouple potentiometer. High purity nitrogen and oxygen gases and compressed air were taken from cylinders. Pure steam was generated in an electric molten salt boiler. The gas pressure and flow rate were adjusted by gas regulators and flow tothameter, respectively. The flow rate of steam introduction into the furnace was controlled by a SAGE Instrument Syringe Pump, while feeding distilled water into the boiler (at 600°C). All gas and steam carrying lines were of stainless steel and heated to about 300°C to prevent any vapor condensation. The sample holder was made of a porcelain crucible perforated at the bottom and hung in the center of the temperature controlled section of the furnace tube by a stainless steel rod. The furnace was heated to the desired temperature prior to sample introduction for firing (Figure 1).

The initial samples were gamma-alumina of 700-850 micrometers (24-20 mesh) and with various specific surface areas. The sample underwent phase transformation under varying conditions of temperature, time of residence and flow rates of gas additives. The heat treated material was cooled gradually at several steps within the furnace and eventually pulled out and poured into a pyrex glass vessel immediately and stoppered to isolate from any vapor adsorption in the atmosphere. The small oxidized metal particles produced from the steel handle of the crucible were then separated by a magnet and the transformed alumina was stored in the sample bottle for appropriate analyses.

Determination of the specific surface areas was periodically performed using a 2200 Micromeritic Surface Area Analyzer. The conversion of alumina over transformation was tested by a Geigerflex D/MAX - 1A, X-Ray Diffractometer whereby the crystalline structure of the transformed alumina and the degrees to which the transformation proceeded were monitored.

Measurements of the percentage of alpha-

alumina on the surface of the transformed sample were performed by the kinetics study of the catalytic dehydration of methanol in the presence of gamma alumina according to the process:



$$\Delta H^\circ_{298} = -23.6 \text{ KJ. mole}^{-1}$$

The reaction is reversible exothermic and is conducted in a fixed bed of gamma alumina catalyst. The reactor was made of a stainless steel tube and fixed in a constant temperature bath. The reaction products were allowed to pass through an electrically heated stainless steel tube via a six-port valco gas sampling valve to a Gow-mac TCD gas chromatograph. The G.C. column was 1.50m long packed by porapack and carbosphere and maintained at 170°C. Carrier gas was hydrogen or helium (Figure 2).

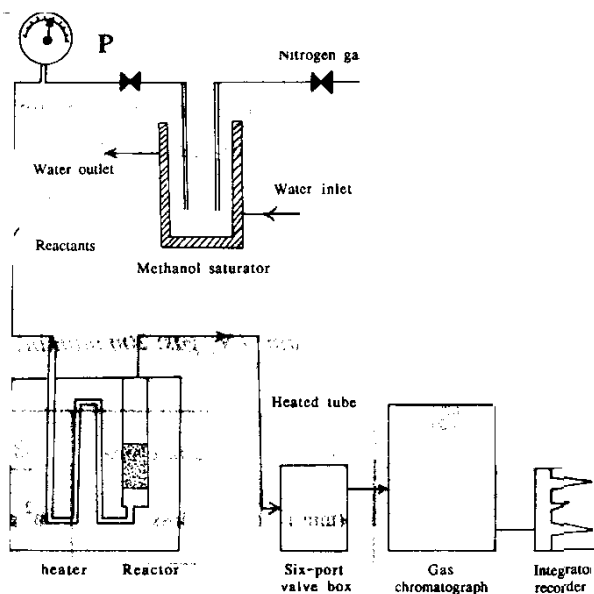


Figure 2. Schematic flow system for the kinetics study of methanol dehydration

RESULTS AND DISCUSSION

The change in the specific surface area of gamma-alumina samples was determined periodically during the heating process. The

kinetics data obtained at temperatures of 1100°C and 1150°C are summarized in Tables 1 and 2. The change in the surface area with time is plotted in Figure 3 and the rate of surface loss with time is plotted in Figure 4.

The variations of the rate of phase-transformation with operating temperatures of 1100-1180°C (in nitrogen atmosphere) and of 750-900°C (in nitrogen and steam atmosphere) have been studied as indicated in Tables 3 and 4 and the results obtained were plotted in Figures 5 and 6. As is seen, the variation of Ln (rate) with reciprocal absolute temperature is linear in the region 750-800°C which deviates from the similar plot in the region 825-900°C (Figures 7 and 8). The same results are observed in the temperature range 1100-1150°C and 1160-1200°C (Figure 9). These observations indicate that the activation energy for the phase transition varies for every 50°C temperature. The activation energies measured are about 65.5 kJ mol⁻¹ (1100-1180°C); 87 kJ mol⁻¹ (750-800°C) and 31 kJ mol⁻¹ (825-900°C).

The bulk density of the processed samples was increased with a loss in surface area. These

observations were at 1125°C and at various time intervals as shown in Figure 10. Thermal calcination of gamma-alumina yields more packing and less porosity in the transformed products.

Under the same conditions of temperature and heating time it is concluded that: (a) nitrogen gas addition produces a product of higher surface area and hence the pores are developed; columns III and VII, and columns VI and VIII in Table 5 indicate this result; (b) steam injection [6] controls the rate of sintering process of alumina; columns III, IV and V in Table 5 show this result; (c) oxygen addition produces a more dense final product with less porosity and surface area, but retards the phase-transformation of alumina.

The yield of the phase-transformation as % alpha-Al₂O₃ formation on the surface of the heated product was investigated by the kinetics measurement in the catalytic dehydration of methanol at 250°C. The mechanistic features of the reaction have been studied by other workers [7-9].

Table 1. Kinetics Data of Gamma-Alumina (S.A.=187.5m²/g) Phase Transformation at 1100°C and Total Pressure of 1 atm. (N₂ gas: 200 ml/min).

Time (min.)	% surface area loss	$-\frac{d(s.A)}{dt}$ m ² .g ⁻¹ /min	product surface area m ² /g	Ln(rate)	Ln(S.A.)
15	41.040	5.131	110.569	1.6353	4.7056
30	72.130	4.509	52.266	1.5061	3.9563
45	77.416	3.226	42.353	1.1712	3.7460
60	81.083	2.534	35.476	0.9298	3.5688
75	89.282	2.232	20.100	0.8029	3.0007
90	93.841	1.955	11.550	0.6706	2.4467

Table 2. Kinetics Data of Gamma-Alumina (S.A.=187.5m²/g) Phase Transformation at 1150°C and Total Pressure of 1 atm. (N₂ gas: 200 ml/min)

Time (min.)	% surface area loss	$-\frac{d(s.A)}{dt}$ m ² .g-1/min	product surface area m ² /g	Ln(rate)	Ln(S.A.)
15	69.610	8.703	56.992	2.1637	4.0429
30	87.028	5.4403	24.326	1.6938	3.1915
45	94.827	3.927	10.826	1.3679	2.3819
60	95.027	2.970	9.325	1.0885	2.2327
75	96.550	2.414	6.470	0.8814	1.8672
90	97.519	2.032	4.652	0.7090	1.5373

Table 3. Temperature Dependence of the Rate of Alumina Phase Transformations. Time of Heating: 30 Minutes. N₂ gas: 200 ml/min. Steam:0

T(°C)	product S.A. m ² /g	10 ⁵ /T (K ⁻¹)	Rate m ² .g-1/min	Ln(rate)
1100	52.266	72.82	4.5089	1.5061
1120	44.815	71.78	4.7573	1.5597
1135	28.778	71.01	5.2919	1.6662
1150	24.326	70.27	5.4403	1.6938
1165	4.530	69.53	6.1001	1.8083
1180	2.151	68.82	6.1794	1.8212

Table 4. Temperature Dependence of the Rate of Alumina Phase Transformations. Time of Heating: 30 Minutes. P_{N₂} = 0.407 atm. P_{H₂O} = 0.593 atm.

T(°C)	product S.A. m ² /g	10 ⁵ /T (K ⁻¹)	Rate m ² .g-1/min	Ln(rate)
750	149.223	97.74	1.2770	0.2445
775	142.000	95.41	1.5178	0.4173
800	135.300	93.18	1.7411	0.5545
825	125.774	91.06	2.0587	0.7220
850	120.900	89.03	2.2211	0.7980
875	115.602	87.10	2.3977	0.8745
900	110.842	85.24	2.5564	0.9386

Table 5. The Influence of Nitrogen Gas and Steam on the Surface Area During Phase Transformation of Alumina at 750-1200°C and 1 atm.

I	II	III	IV	V	VI	VII	VIII	IX
N ₂ (ml/min)	200	200	200	200	400	0	100	
steam(ml/min)	0	0.17	0.50	0.80	2.5	0.17	2.5	
T(°C)	Surface area (m ² .g ⁻¹)							Time (min)
750	-	162.600	-	149.233	155.211	154.610	145.606	30
750	-	154.585	-	-	-	148.217	-	60
800	-	150.070	-	135.300	139.547	138.040	135.280	30
800	-	145.690	-	-	-	131.644	-	60
850	-	141.230	-	120.900	123.381	128.091	121.405	30
850	-	138.480	-	-	-	126.034	-	60
900	-	-	125.000	122.233	119.236	-	-	15
900	-	128.500	117.344	110.842	110.051	117.500	106.876	30
900	-	-	-	107.650	107.672	112.160	-	45
900	-	118.785	114.009	104.526	105.397	106.988	-	60
900	-	-	-	101.477	103.580	-	-	75
900	-	-	110.489	-	101.661	-	-	90
900	-	-	105.000	-	101.485	-	-	120
925	-	-	-	-	105.117	-	-	30
950	-	-	-	-	98.192	-	97.645	30
975	-	-	-	-	96.383	-	-	30
1000	-	-	-	-	84.553	-	85.649	30
1050	-	-	-	-	-	-	75.043	30
1100	52.266	-	-	-	56.501	-	44.437	30
1120	44.815	-	-	-	52.652	-	40.560	30
1135	28.778	-	-	-	48.266	-	27.200	30
1150	24.326	-	-	-	43.072	-	18.825	30
1165	4.530	-	-	-	37.960	-	4.020	30
1180	2.151	-	-	-	16.132	-	3.500	30
1200	2.006	-	-	-	8.110	-	2.140	30

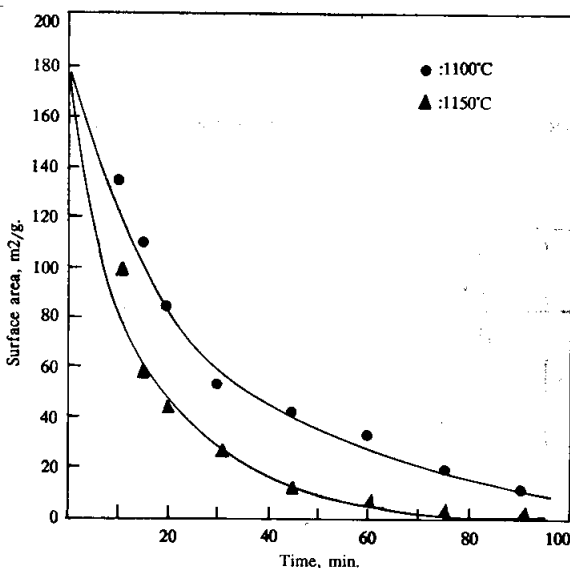


Figure 3. The variation of specific surface area of transformed alumina with time.

N₂=200 ml/min. ●: T=1100°C. ▲: T=1150°C.

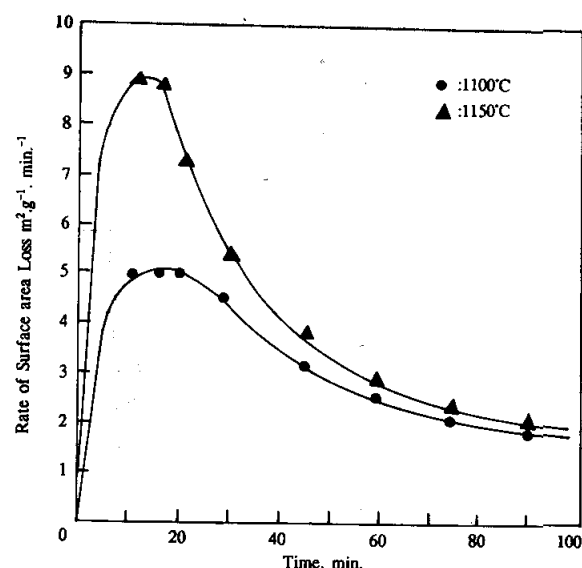


Figure 4. The rate-time curves for surface area change in alumina phase-transformation

N₂=200ml/min. ●: T=1100°C. ▲: T=1150°C.

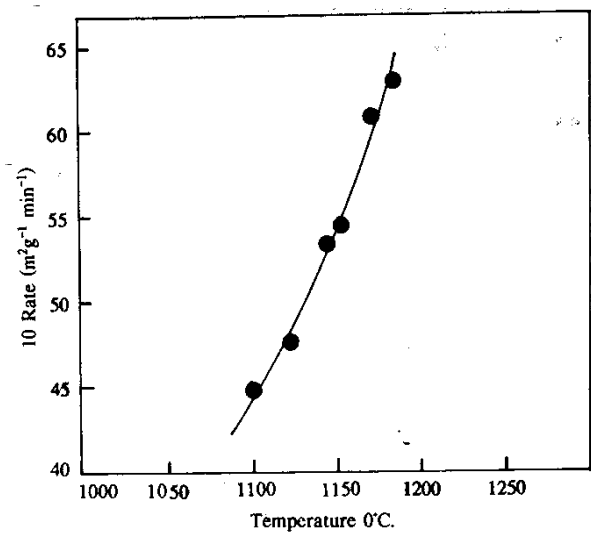


Figure 5. Rate-temperature dependence for alumina phase transformation in nitrogen atmosphere at 1100-1180°C.

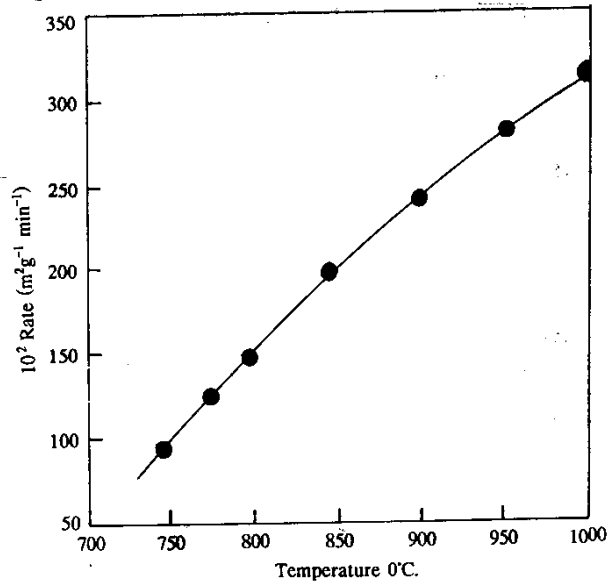


Figure 6. Rate-temperature dependence for alumina phase transformation at 750-1000°C.
 $P_{N_2} = 0.407 \text{ atm.}$, $P_{\text{steam}} = 0.593 \text{ atm.}$

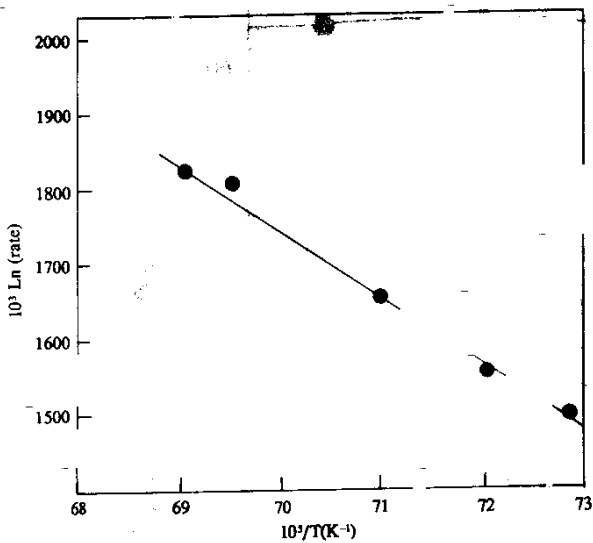


Figure 7. Rate-temperature plot for alumina phase transformation in nitrogen atmosphere.

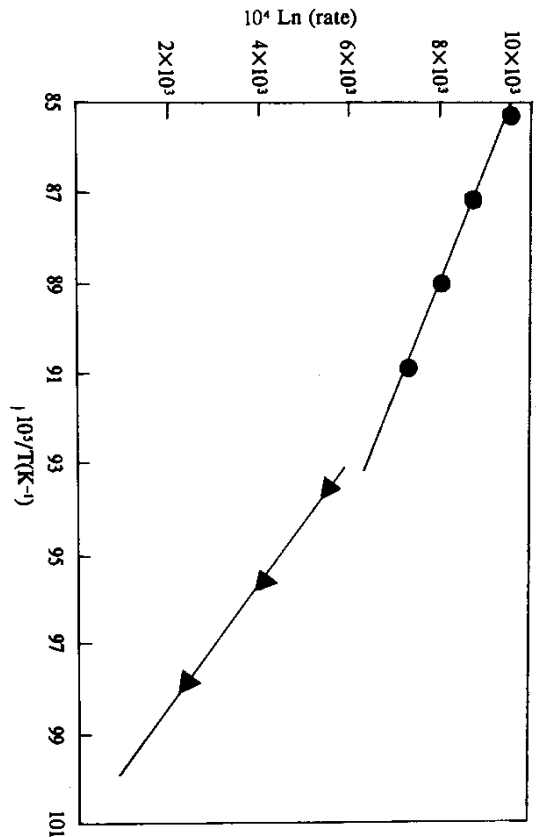


Figure 8. Rate-temperature plot for alumina phase transformation at $P_{N_2} = 0.219 \text{ atm.}$,
 $P_{\text{steam}} = 0.781 \text{ atm.}$

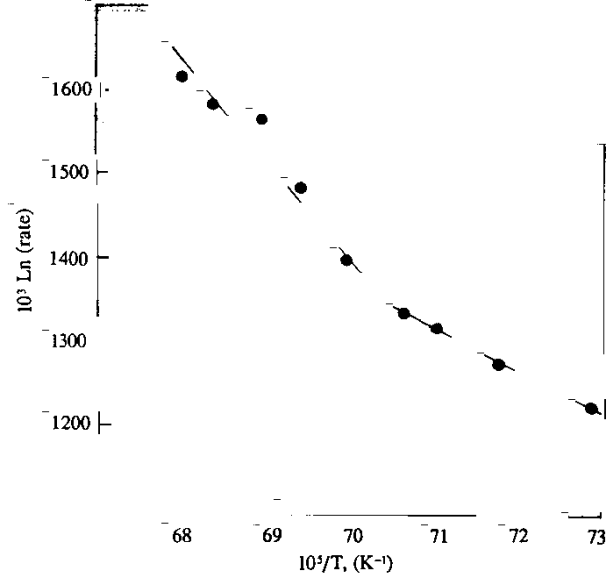


Figure 9. Rate-temperature dependence for alumina phase transformation at 1100-1200°C. $P_{N_2} = 0.219$ atm. $P_{\text{steam}} = 0.781$ atm.

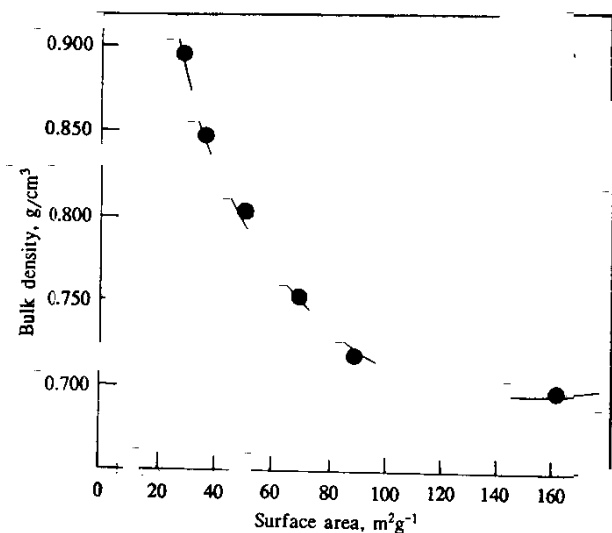


Figure 10. Variation of the bulk density with surface area of alumina at 1125°C and various time intervals.

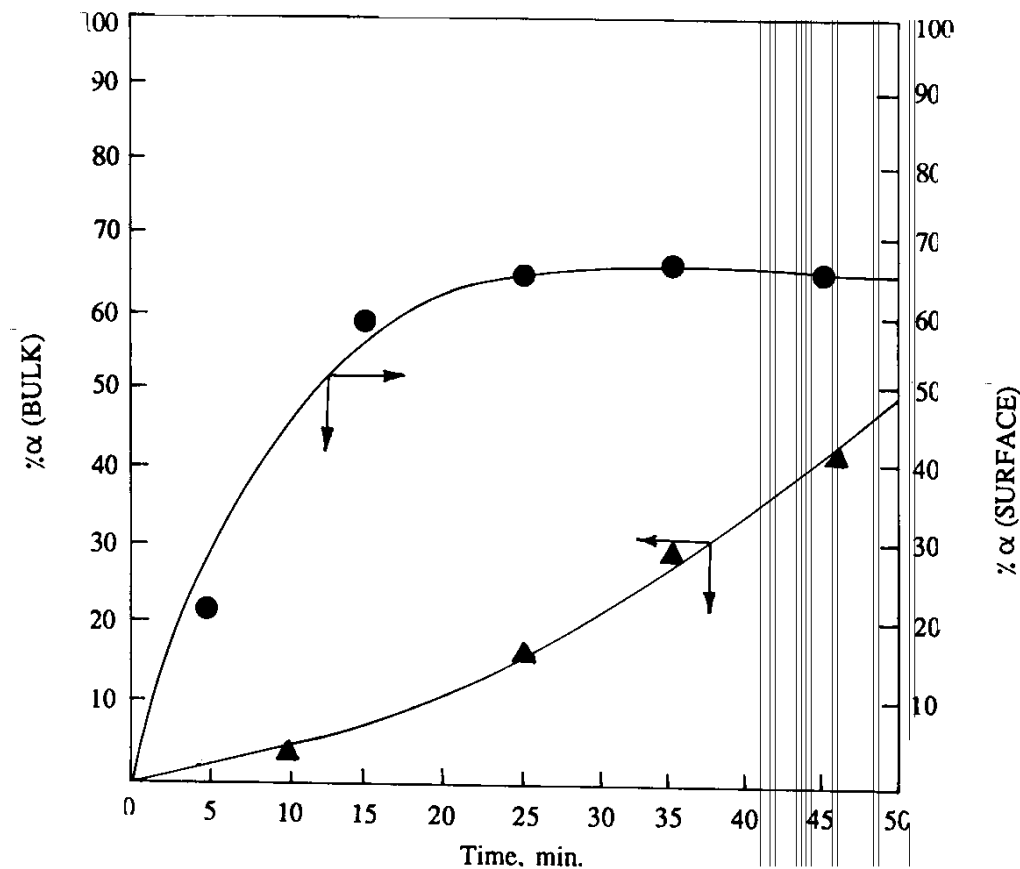


Figure 11. Variation of the phase transformation yield with time for alumina at 1100°C.

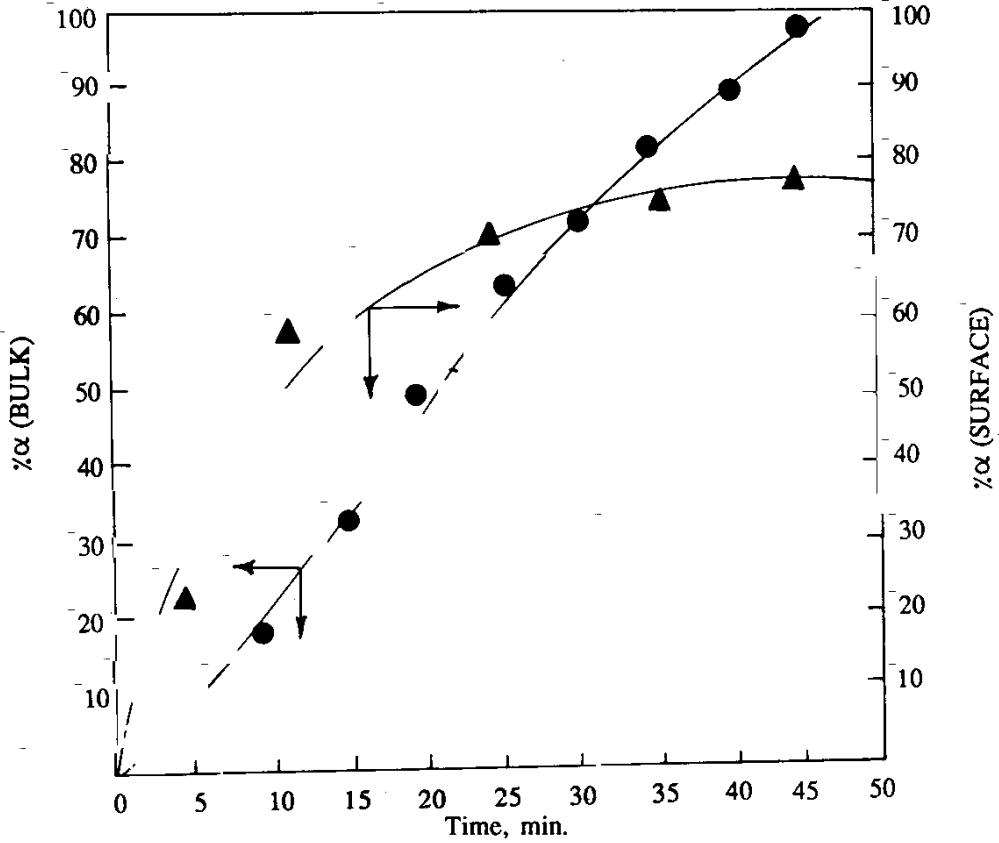


Figure 12. Variation of the phase transformation yield with time for alumina at 1125°C.

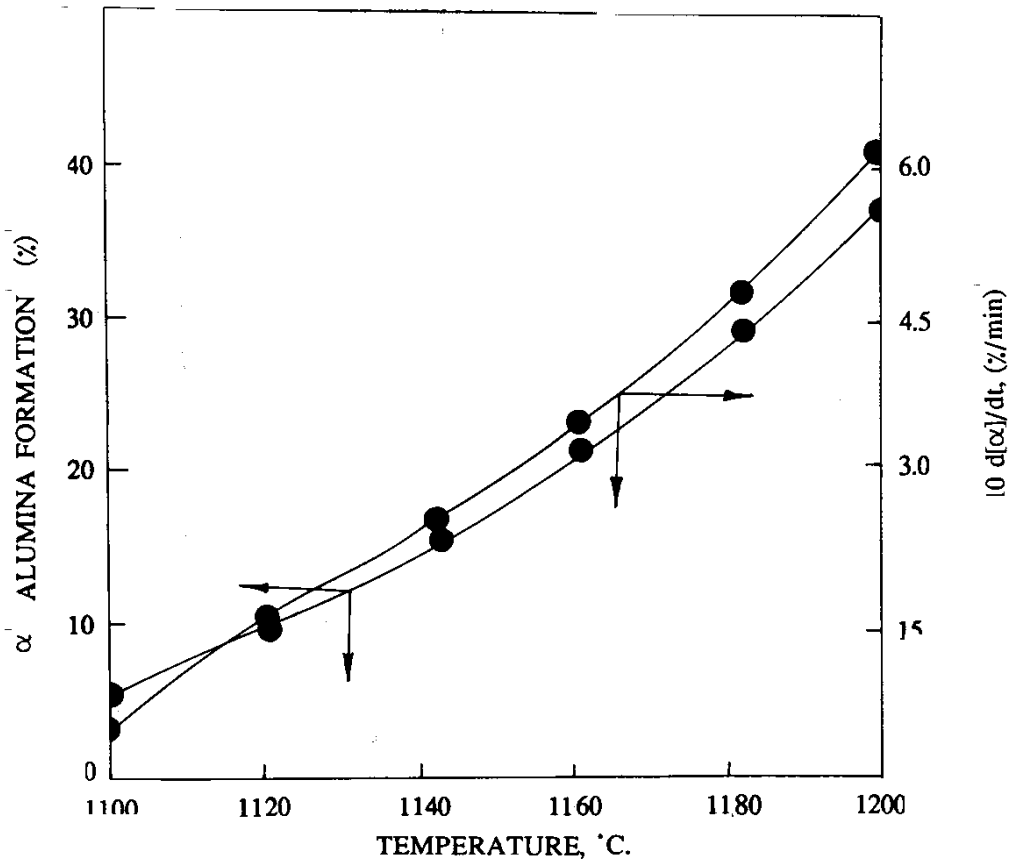


Figure 13. The variation of % alpha-alumina with temperature during phase transformation of gamma-alumina in nitrogen atmosphere. Transformation time: 1 hour.

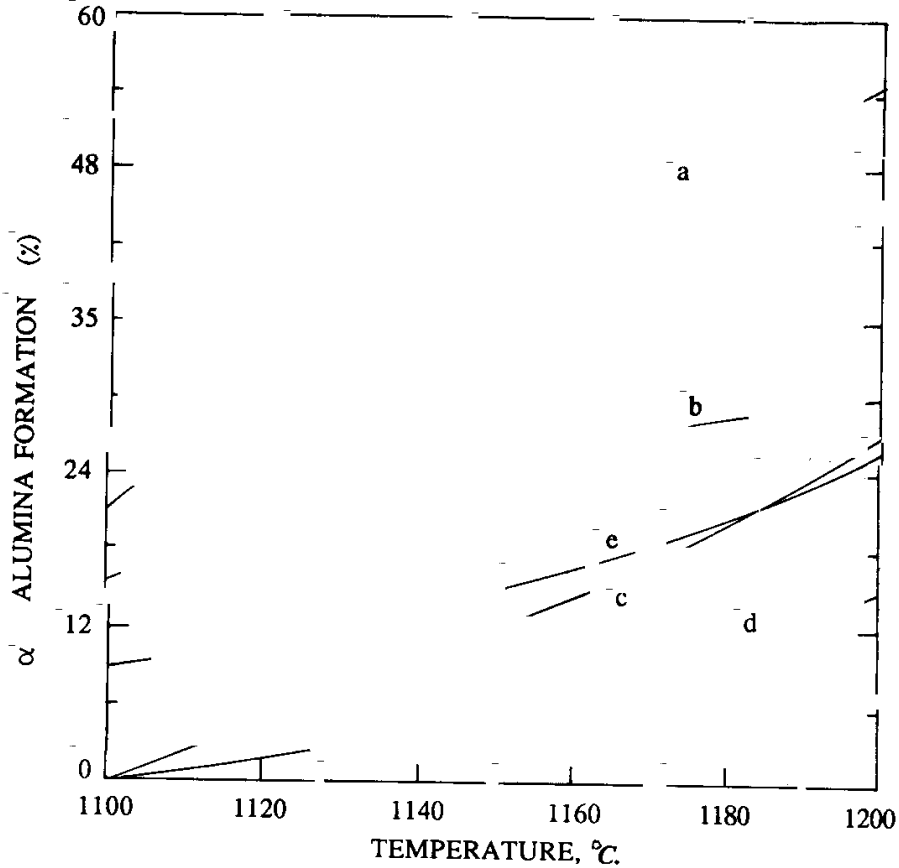


Figure 14. The variation of % alpha-alumina formation with temperature at atmospheric pressure. (a) $P_{steam} = 1atm.$ (b) $P_{N_2} = 0.35atm., P_{steam} = 0.65atm.$ (c) $P_{air} = 1atm.$ (d) $P_{O_2} = 1atm.$ (e) $P_{O_2} = 0.5atm., P_{steam} = 0.5atm.$

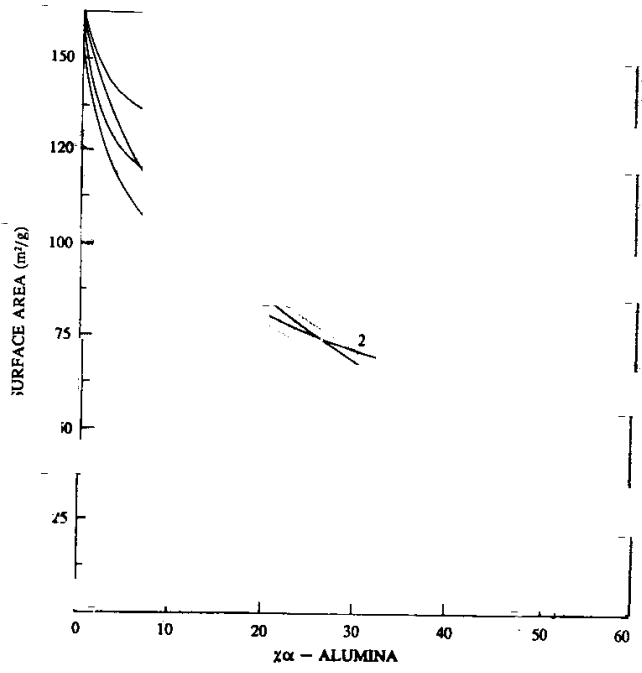


Figure 15. The variation of surface area of transformed alumina with the percentage conversion at 1atm. and temperatures 1100-1200°C. (1) $P_{N_2} = 1atm.$ (2) $P_{steam} = 1atm.$ (3) $P_{N_2} = 0.350atm., P_{steam} = 0.65atm.$ (4) $P_{air} = 1atm.$

Table 6. Kinetics Data of Methanol Dehydration Catalytic Process for Determination of the Percentage Alpha-alumina Formed on the Surface of Transformed Alumina.

Sample Number	gamma alumina	11A	11C	11E	11G	11I	14A	14B	14E	14G	14I	15B
Surface area (m ² /g)	160.684	90.513	66.367	58.357	54.068	49.750	87.234	68.314	47.985	35.879	28.690	21.262
Bulk density (g/cm ³)	0.7012	0.6894	0.7325	0.7478	0.7587	0.7643	0.7234	0.7579	0.8149	0.8587	0.8914	0.8800
Rate constant, k (lit.mol ⁻¹ .sec ⁻¹)	4.2842	1.8462	0.7520	0.5719	0.5298	0.4853	1.8350	0.9222	0.4445	0.3092	0.2334	0.0864
$10^6(K/S_{BET})$	26662	20397	11331	9800	9799	9755	21035	12164	9263	8617	8135	4064
$10^6\theta_{\gamma} = \frac{(K_i/S_{BET})_{trans}}{(K_i/S_{BET})_{\gamma-Al_2O_3}}$	10 ⁶	765021	425000	367564	367527	365876	788951	456245	347423	323194	305116	152427
$\alpha\%$ (surface) = (1 - θ_{γ})100	0	23.50	57.50	63.24	63.25	63.41	21.10	54.37	65.26	67.68	69.50	84.76
Time of transformation (min)		5	15	25	35	45	5	10	25	35	45	75
Heating temperature (°C)		1100	1100	1100	1100	1100	1125	1125	1125	1125	1125	1135

$10^6K = \frac{10^6K}{\rho_{S_{BET}}} \left(\frac{\text{lit}^2 \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}}{\text{m}^2} \right)$	38023.4	29586.6	15468.9	13105.1	12915.5	12763.3	29078.0	16049.6	11367.0	10034.9	9126.1	4618.2
$10^6\theta_{\gamma} = K'_{trans} / K'_{\gamma-Al_2O_3}$	10 ⁶	778116	406827	344659	339672	335670	764740	422098	298947	263914	240013	121457
$\alpha\%$ (surface) = (1 - θ_{γ})100	0	22.19	59.32	65.54	66.03	66.43	23.53	57.79	70.11	73.61	76.00	87.86
Time of transformation (min)		5	15	25	35	45	5	10	25	35	45	75

Let K_γ = rate constant associated with gamma-alumina of BET- surface area S_γ

K_t = rate constant associated with transformed alumina of BET - surface area S_t

θ_γ = the ratio of K_t/S_t to K_γ/S_γ or

$$\theta_\gamma = \frac{(K_t) (S_\gamma)}{(K_\gamma) (S_t)}$$

then, $\theta_\alpha = 1 - \theta_\gamma$ = the fractional contribution of alpha on the surface of transformed alumina.

The rate constants K , were computed from the kinetics developed by other authors [10, 11 and 12]. The results obtained are summarized in Table 6.

The transformed aluminas at 1100°C and 1125°C exhibit different percentages of alpha- Al_2O_3 formation as shown in Figures 11 and 12. The variations of % alpha alumina formed with temperature in nitrogen atmosphere and also in the presence of steam, air, oxygen and mixtures of ($\text{N}_2 + \text{H}_2\text{O}$) and ($\text{O}_2 + \text{H}_2\text{O}$) within a period of one hour are indicated in Figures 13 and 14. The change of the specific surface area of the final transformed product with the % alpha- alumina formed was computed and plotted in Figure 15.

CONCLUSION

Conversion of various aluminas from one phase to another requires specified physical and atmospheric conditions. Since the catalyst supports are recognized by their characterization, the presence of foreign additives controls such properties to produce desired final materials. Successive X-ray diffraction, surface

area and pore volume, and measurements of the % α - alumina on the surface of the product lead to the performance of the various industrial alumina supports.

Among the catalyst supports, aluminas exhibit numerous applications in the organic processes. The alpha type is widely used in the controlled chemical reactions such as selective oxidation of low molecular weight hydrocarbons. High selectivity appears in the transformed material when starting alumina is thermally treated at temperatures below the sintering state; hence using exact gas flow rates and temperatures in the heating system of aluminas yields satisfactory final materials that might be applied in certain catalyst preparation processes.

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