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Alumina and Synthesis Intermediates Derived from Diethylaluminum Amide, Benzaldehyde and Water

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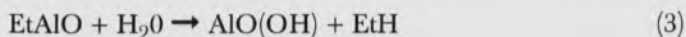
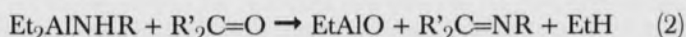
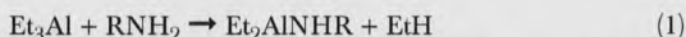
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Abstract

The reaction of diethylaluminum amide $[\text{Et}_2\text{AlNH}_2]$ with benzaldehyde in toluene produces a solution of ethylaluminumoxane polymer $[\text{EtAlO}]$ and hydrobenzamide $[\text{PhCH}=\text{NCH}(\text{Ph})\text{N}=\text{CHPh}]$. Alumina then is precipitated by the addition of water. Transition aluminas that may be useful in heterogeneous catalyst applications are obtained after calcining. Details of the chemistry of solution intermediates according to ^1H NMR and the properties of the alumina product according to surface area analyses and powder x-ray diffraction are described.

Introduction

Porous aluminas are valued as primary catalysts or as promoter supports for noble metal catalysts (Heck and Farrauto, 1995; Rase, 2000). Previously we reported a method to prepare porous alumina from precursors synthesized by a series of reactions with alkylaluminum derivatives (Lindquist et al., 1996; Lindquist and Rooke, 2000). The general synthetic method involves three principal steps. Combination of triethylaluminum with a primary amine or ammonia in hydrocarbon solvent yields a diethylaluminum amide and an equivalent of ethane gas. An aldehyde or ketone then is added to produce ethylaluminumoxane polymer, an imine, and a second equivalent of ethane. Addition of water results in precipitation of alumina precursor and a third equivalent of ethane. A generalized stoichiometry to prepare an aluminum oxide hydroxide precursor is shown by Equations (1)-(3).



There are a number of variables possible in the synthesis scheme. For example, addition of two equivalents of water, in lieu of one equivalent by Equation (3), gives a precursor stoichiometry of $\text{Al}(\text{OH})_3$ instead of $\text{AlO}(\text{OH})$. Other potential variables include the use of different amines and aldehydes or ketones as reagents for Equations (1) and (2). Additionally, the imine product of Equation (2) may be subject to byproduct chemistry depending on its composition and on synthesis conditions. Herein we report details of the chemistry of intermediates when ammonia and

benzaldehyde are used as reagents in Equations (1) and (2) respectively. The properties of the alumina obtained after calcining are compared with those of a commercial alumina.

Materials and Methods

Syntheses involving triethylaluminum or its derivatives were conducted under N_2 or Ar atmosphere with an oil bubbler purge using Schlenk techniques. Benzaldehyde was obtained after two distillations in argon atmosphere. Triethylaluminum as a 25 wt% solution in toluene and Proton Sponge® [1,8-bis-(dimethylamino)naphthalene] were used as received (Aldrich Chemical Co.). Anhydrous NH_3 from a cylinder (Delta Air Gas) was dried by passing it through a glass column containing KOH pellets. A commercial pseudoboehmite alumina was obtained (Alcoa Hi-Q 30) for purposes of comparison with aluminas synthesized.

The typical synthesis of an $\text{Al}(\text{OH})_3$ precursor using 2 equivalents of water is as follows. A 120 mL (0.23 mol) portion of 1.9M Et_3Al in toluene was transferred by cannula to a 250 mL Schlenk vessel equipped with a water reflux condenser, septum inlet, and N_2 bubbler. Warning: Triethylaluminum is pyrophoric and must be handled using appropriate precautions. Anhydrous NH_3 was bubbled with a needle through the septum into the stirred solution maintained at 70°C . When gas evolution ceased, indicating reaction completion to form diethylaluminum amide $[\text{Et}_2\text{AlNH}_2]$, the flask was cooled to 0°C in a water ice bath and NH_3 addition discontinued. With continued stirring, one equivalent of benzaldehyde (23.2 mL, 0.23 mol) was introduced by syringe over a period of 30 minutes. This was accompanied by vigorous ethane gas evolution. When the benzaldehyde addition was complete, the solution again was saturated with NH_3 . With continued stirring, two equivalents of water (8.3 mL, 0.46 mol) were introduced by

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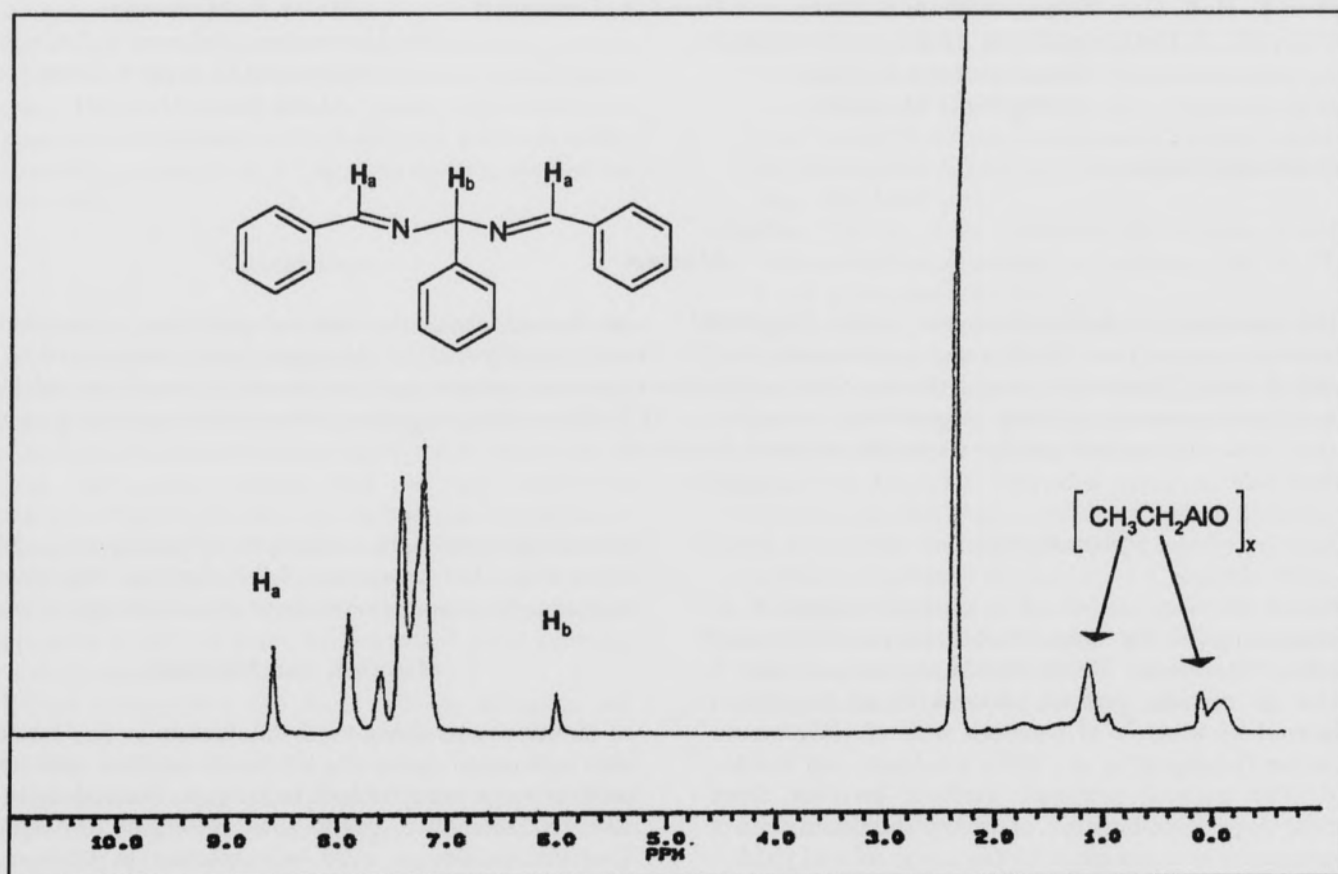


Fig. 1. ^1H NMR spectrum of ethylaluminosiloxane and hydrobenzamide in toluene, proximate composition $[\text{EtAlO}]_{1.0}[\text{PhCH}=\text{NCH}(\text{Ph})\text{N}=\text{CHPh}]_{0.33}$.

syringe over a period of 30 minutes accompanied by gas evolution and precipitation of alumina precursor. Excess NH_3 was bubbled through the cold solution to saturate it. The flask was removed from the ice bath, capped with a loosely fitted stopper, and allowed to stand undisturbed for four days at room temperature. After four days, the alumina was filtered from the supernatant and washed with two 50 mL portions of toluene. Hydrobenzamide, recrystallized from diethyl ether, was recovered in 50% yield (11.4 g) from the evaporated supernatant filtrate and toluene washings (m.p. 101°C , literature same) (Strain, 1927). ^1H NMR of hydrobenzamide (CDCl_3) δ 6.0 (s, 1 H), 7.2-7.5 (m, 13 H), 7.8-7.9 (m, 2 H), 8.6 (s, 2 H) ppm; ^{13}C NMR δ 92.9, 127.5, 128.1, 128.8, 128.9, 131.3, 136.2, 160.9 ppm. Mass Spectrum (70eV) [m/e (relative intensity)]: $[\text{M}^+]$ 224 (5), 194 (100), 167 (10), 152 (3), 116 (16), 106 (10), 91 (80), 77 (20), 65 (13), 51 (19), 39 (13), 27 (12).

Alumina was calcined in a porcelain crucible in a muffle furnace. The atmosphere was humidified by bubbling air through a water containing gas dispersion bubbler at 50°C before passing the air into the furnace. The flow rate of air through the bubbler was sufficient to replace the furnace atmosphere a minimum of 2 times per minute. The temperature was ramped at a rate of $5^\circ\text{C}/\text{minute}$ to a specified temperature and held for 3 hours before turning off the furnace.

The characterization methods employed for the alumina and precursors are as follows. Solutions during syntheses were monitored by ^1H NMR using a Bruker 200 MHz FTNMR. The air and moisture sensitive NMR samples were prepared by repeated freeze-pump-thaw and glass sealed under vacuum with a torch. Hydrobenzamide, isolated from the product supernatant and recrystallized, was characterized by ^1H and ^{13}C solution NMR as well as

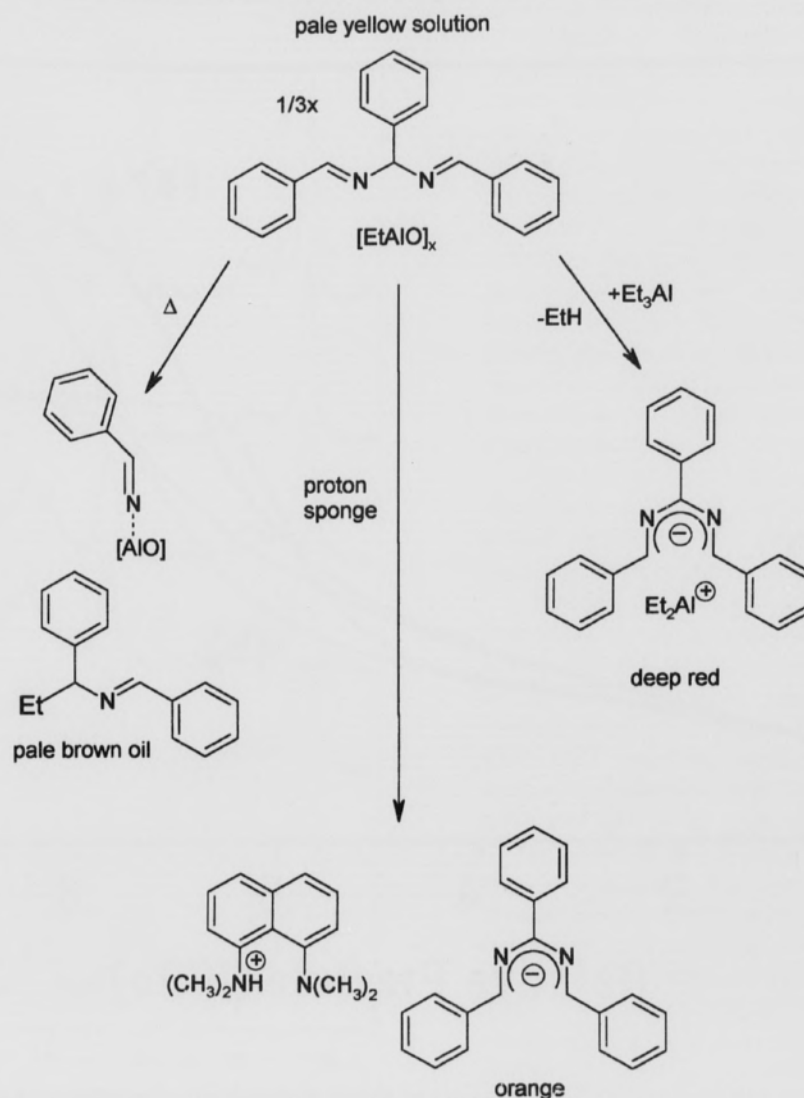
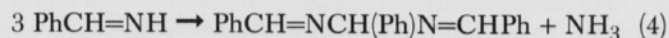


Fig. 2. Chemical transformations of hydrobenzamide under different conditions.

by mass spectrometry (Hewlett Packard 5890 series II GC with 5970 series mass selective detector) at 70 eV. Surface analyses of calcined alumina by N_2 adsorption and desorption isotherms were obtained with a NOVA-1200 gas physisorption instrument (Quantachrome Corp.). BET specific surface areas were calculated from 5 points of the adsorption branch of the isotherm ($0.05 \leq P/P_0 \leq 0.30$). Samples were outgassed overnight under vacuum at 250°C prior to surface analyses. X-ray powder patterns were obtained using a Rigaku Geigerflex x-ray generator equipped with a theta-theta goniometer and sample rotator (step size $0.05^\circ 2\theta$, 1 second per step, range 10° to $75^\circ 2\theta$).

Results and Discussion

Imine Chemistry.—Imines derived from ammonia are sensitive to further condensation (Layer, 1963). Thus, the isolated imine in this study was not benzylimine (PhCH=NH) which was expected from benzaldehyde according to Equation (2). Instead, hydrobenzamide [$\text{PhCH=NCH(Ph)N=CHPh}$] was recovered from the supernatant after precipitation of the alumina. Hydrobenzamide is the condensate of three benzylimine equivalents according to Equation (4).



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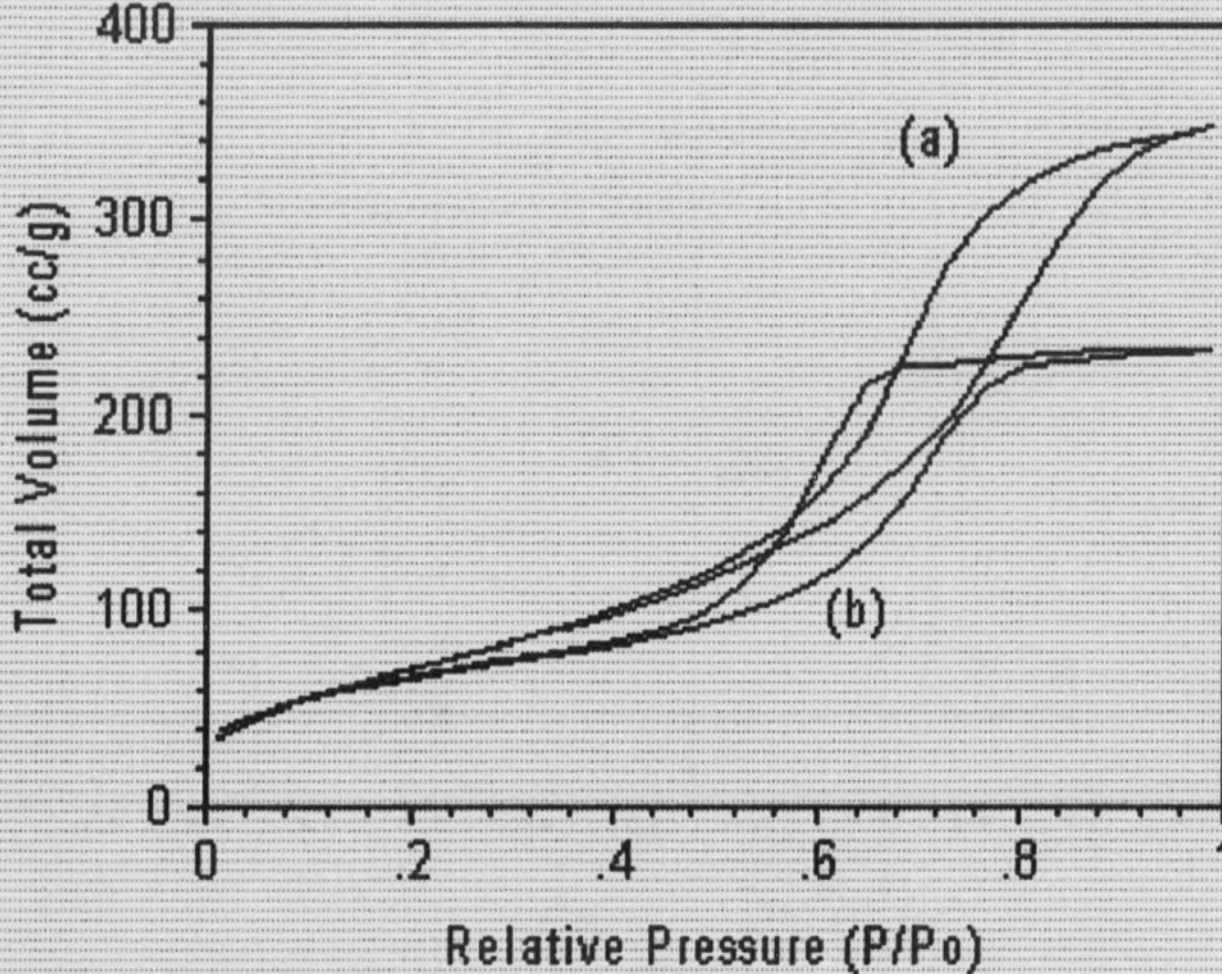


Fig. 3. N₂ isotherms of aluminas calcined at 500°C for 3 hours in steam atmosphere a.) synthesized alumina b.) commercial alumina (Alcoa HiQ-30).

Analysis of the reaction mixture prior to alumina precipitation with water also confirmed the presence of hydrobenzamide at this stage of the synthesis. Figure 1 is the ¹H NMR spectrum of an aliquot collected after addition of one equivalent of benzaldehyde to the solution of diethylaluminum amide [i.e. completion of Equation (2)]. The broad resonances at 1.3 and 0 ppm in Fig. 1 correspond to the ethyl functions of the [EtAlO] polymer. The large singlet at 2.3 ppm is the methyl of toluene solvent. The signals from hydrobenzamide range from 6.0 to 9.6 ppm. Of particular interest is the acidic hydrogen of the central carbon of hydrobenzamide (H_b) seen at 6.0 ppm.

The acidic nature of hydrobenzamide has been found to promote byproducts if synthetic conditions deviated from

those typically used as described in "Materials and Methods" above. Figure 2 summarizes our findings to date concerning these byproducts. The top of Fig. 2 shows the normal solution composition during a typical synthesis based on the NMR data presented in Fig. 1. If, however, the reaction medium is not kept cool during either the addition of benzaldehyde or the subsequent water addition, the solution turns a brown color. NMR and mass spectrometry analysis confirmed the presence of the thermal decomposition products shown on the left side of Fig. 2. Under another set of synthesis conditions, the right side of Fig. 2 shows what we found to be the most striking manifestation of the acidic properties of hydrobenzamide. The color changes from pale yellow to deep red when

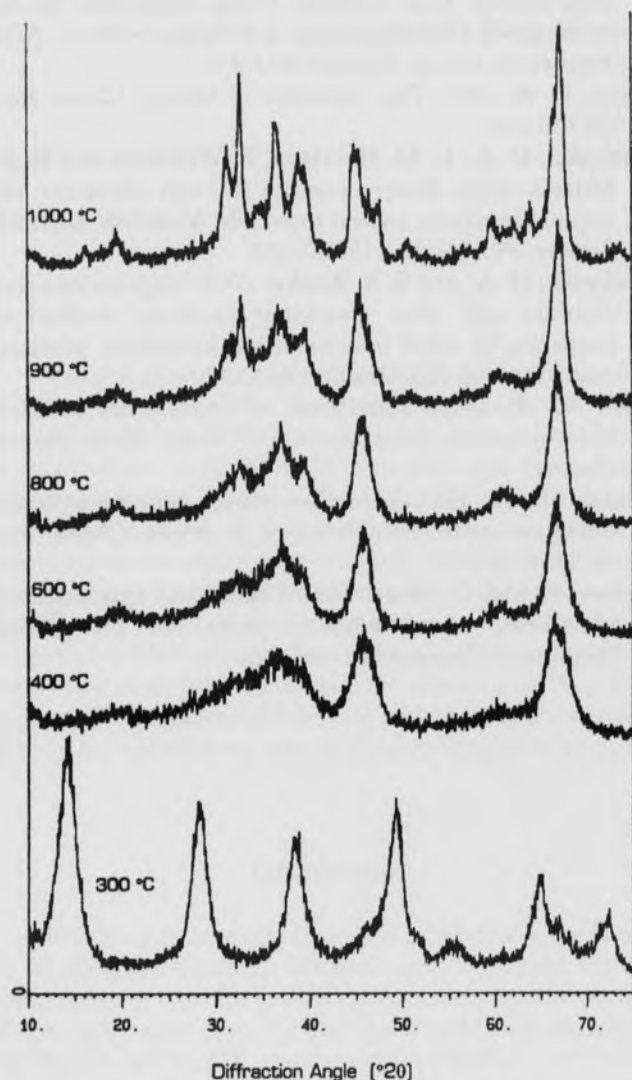


Fig. 4. Powder x-ray diffraction patterns for Alcoa HiQ-30 alumina calcined at various temperatures.

triethylaluminum. (Et_3Al) is added to the solution containing hydrobenzamide. The deprotonated aromatic anion of hydrobenzamide was implicated (Hunter and Sim, 1969). We tested this assumption by adding the nonchelating base, Proton Sponge® [1,8bis-(dimethylamino)naphthalene], instead of Et_3Al . This also resulted in a strong color change, and as ^1H NMR analysis confirmed, loss of the proton of the central carbon (H_b of Fig. 1) of hydrobenzamide. The byproducts of hydrobenzamide illustrated in Fig. 2, although interesting, are to be avoided in order to produce an

alumina containing a minimum of organic impurities.

Alumina Properties.--Despite complications of byproducts, hydrobenzamide appears to exert a positive effect on alumina properties and may do so by functioning as a chelate during precipitation of the alumina. Relevant to our studies, Zeng and coworkers maximized the surface area for an alumina precipitated from an aluminum alkoxide precursor by coaddition of 1/3 equivalents of acetylacetonate, a bidentate chelate (Ji et al., 2000). The authors asserted that chelate coordination to aluminum centers induced defects in the alumina microstructure during precipitation. Moreover, they showed that additions of greater or lesser quantities of acetylacetonate were not as effective as 1/3 of an equivalent to enhance surface area. Coincidentally in our system, hydrobenzamide is formed in a ratio of 1/3 equivalents relative to aluminum. The serendipitous match of the ratio in our preparation with that found optimum by Zeng may help to explain the exceptional properties of our alumina.

Indeed, Fig. 3 shows the N_2 adsorption and desorption isotherms for our synthesized alumina and for Alcoa alumina, both calcined in steam atmosphere for three hours at 500°C. The larger pore volume of our alumina in comparison to the commercial alumina is readily apparent. The BET specific surface areas calculated for the synthesized alumina and Alcoa calcined alumina were 296 m^2/g and 228 m^2/g , respectively.

In addition to having a high pore volume and surface area, it is desirable that alumina in catalysts be resistant to crystallization at elevated temperature. Crystallization results in a coarsened microstructure and diminished catalyst activity. Figure 4 illustrates the phase changes of the Alcoa Hi-Q 30 alumina, which typify a boehmite type precursor. The alumina maintains a boehmite [$\text{AlO}(\text{OH})$] phase after calcining at 300°C for three hours. At 400°C a phase change to $\theta\text{-Al}_2\text{O}_3$ occurs, and at higher temperatures, two indiscreet phase changes to $\delta\text{-Al}_2\text{O}_3$ and finally $\gamma\text{-Al}_2\text{O}_3$ at 1000°C are observed in Fig. 4. Temperatures and associated phases apparent from the patterns in Fig. 4 are consistent with those reported in the literature (Wefers and Misra, 1987). By contrast, the diffraction patterns of our alumina shown in Fig. 5 indicate a substantially more amorphous material at similar temperatures. After calcining to 1000°C a $\gamma\text{-Al}_2\text{O}_3$ phase is still retained, which is truly exceptional.

Based on favorably high pore volume, high surface area, and low crystallinity we are optimistic that our aluminas may supplant commercial aluminas in some applications. Studies are now underway to examine this potential for automobile emissions catalytic convertors. In addition we continue to seek further improvements in alumina microstructure and thermochemical stability through modified synthesis variables.

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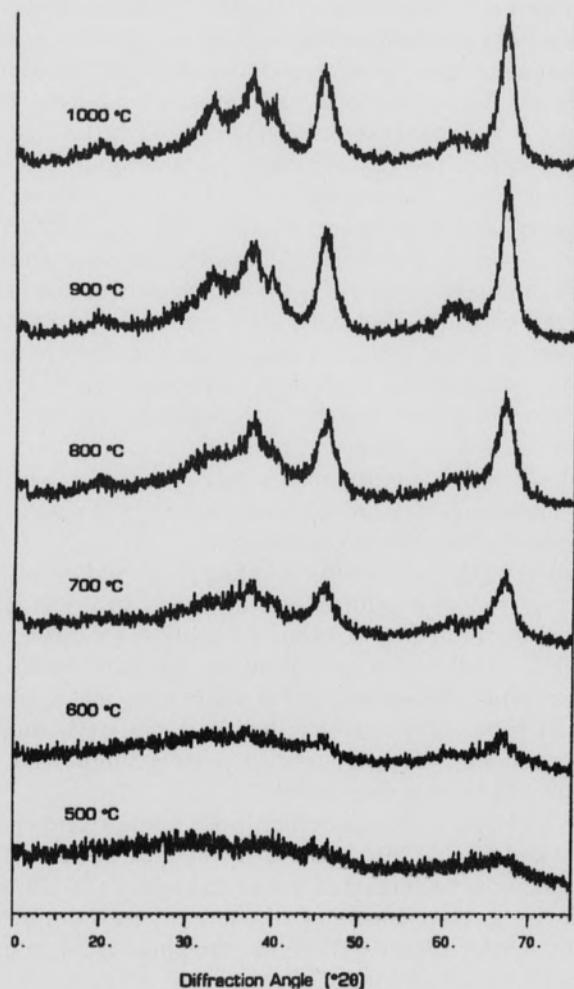


Fig. 5. Powder x-ray diffraction patterns for our synthesized alumina calcined at various temperatures.

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