JOURNAL OF CATALYSIS 117, 42–51 (1989)

Surface Characterization of Amorphous Alumina and Its Crystallization Products

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Received November 12, 1987; revised September 26, 1988

A nonconventional method, based on the thermal decomposition of aluminum nitrate in the presence of a suitable reducing agent, was applied to the preparation of amorphous alumina with high surface area. Modified aluminas were obtained in a further step by hydration and crystallization of the amorphous form. The characteristics of all these materials were investigated by XRD, DTA, and FT-IR spectroscopy. The presence of surface acidic sites was examined with the aid of pyridine as an adsorbed probe molecule. The catalytic properties of the materials were tested using as a probe reaction the dehydration of methanol to dimethyl ether at temperatures between 450 and 560 K. The results of catalytic tests and surface characterization of the materials are discussed in terms of three different Al^{3+} cationic sites. © 1989 Academic Press, Inc.

INTRODUCTION

Aluminas constitute a family of materials whose importance in the field of heterogeneous catalysis is enormous and constantly growing (*1*). The solid state chemistry of aluminum oxides is very complex, several different metastable crystal phases being formed under different conditions (*2, 3*). All of these transform at high temperature into the most thermodynamically stable form, α-Al_2O_3 (corundum).

"Transition aluminas" with cubic structures, notably γ-Al_2O_3 and η-Al_2O_3, may be prepared with high to very high surface areas and find many applications as catalysts or active catalyst supports (*4*). α-Al_2O_3, usually obtainable with a surface area not exceeding 50 m^2/g, also finds application as an inert mechanically very strong support for metal (especially silver) catalysts (*4*).

Amorphous aluminas are also known and may be prepared as precursors of transition aluminas; these have been claimed to be interesting catalytic materials in their own right (*5*). Significant efforts have been devoted, particularly by Teichner and coworkers (*6–8*), to prepare high-surface-area amorphous aluminas. It has recently been proposed that significant amounts of amorphous phases may be present on high-surface-area transition alumina preparations (*9*). However, very few data are reported in the literature on the surface properties of amorphous alumina and on its role in catalytic behavior.

Although the surface chemistry of aluminas has been extensively investigated (*10–13*), the nature of the surface sites is still far from clear, as recently pointed out by Zecchina *et al.* (*14*). Recently in one of our laboratories a method was developed for the preparation of high-surface-area amorphous aluminates (*15, 16*). This method may be successfully applied to the preparation of amorphous alumina and, following its crystallization, of chlorine-free and alkali-metal-free transition aluminas and corundum powders. This paper describes the preparation and surface characterization of these materials.

0021-9517/89 $3.00

EXPERIMENTAL METHODS

a. Materials and Instrumentation

Aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$], tartaric acid, and methanol were reagent-grade products from Carlo Erba (Milano, Italy). Pyridine was a purer product from Carlo Erba (Milano, Italy) and was further purified by multiple freeze–pump–thaw cycles before vaporization.

Differential thermal analysis (DTA) was performed with a Netzsch 404 DTA cell equipped with a computerized 434 programmer unit. X-ray powder diffraction (XRD) analyses were performed with computer-aided Philips PW 1710 equipment. Infrared spectra were recorded with a Nicolet MX1 Fourier transform spectrometer, equipped with conventional gas-manipulation and an evacuation ramp. Samples for study (alumina) were pressed into self-supporting disks and pretreated by heating under dynamic evacuation (10^{-5} Torr for 2 h) in the IR cell.

b. Sample Preparation

The preparation of amorphous alumina was based on a widely applicable procedure developed by some of the present authors with the aim of obtaining high-surface-area ceramic powders which are easy to sinter. This method consists of a low-temperature thermal decomposition of nitrate or nitrate mixtures of different metals, sustained by the simultaneous oxidation of a suitable organic reducing agent. More specifically, tartaric acid is added (about 10 wt%) to aluminum nitrate and the resulting mixture is heated to 373 K until it completely melts. The resulting liquid is then heated directly to 453 K. Under this condition a vigorous evolution of gas (NO_x, CO_2, H_2O_{vap}) takes place, resulting in the formation of a brown-greenish solid, probably so colored because of the presence of residues of nitrogen oxides. A final heat treatment to 673 K (2 h) allows one to remove the last traces of NO_x and to accomplish the transformation to a product, which is a white, soft solid characterizable (see later) as amorphous alumina (sample A).

Samples of hydrated alumina were obtained from this amorphous alumina A by hydrothermal treatment. About 10 g of amorphous alumina were mixed with 200 ml of water and magnetically stirred at room temperature. The open vessel was thereafter transferred to a furnace at 383 K and heated until completely dry (about 15 h). XRD analysis of the material obtained in this way (designated as sample B) produced a pattern (Fig. 1) which is typical of pseudoboehmite.

c. Catalytic Measurements

The catalytic activity of the alumina samples was tested by isothermal runs of methanol dehydration to dimethyl ether in a tubular reactor. Liquid methanol from a metering pump was mixed in a vaporizer in known proportions with a gaseous stream of inert diluting gas (helium or nitrogen) and the mixture was passed to a stainless-steel reactor containing a fixed bed of alumina. The reactor was electrically heated and the catalyst temperature was monitored through two thermocouples placed at the ends of the cylindrical bed of alumina. The bed occupied 0.6 ml in volume and was composed of particles 0.5–1 mm in size obtained by crushing a pressed self-consistent sheet of material.

In a typical run the catalyst was conditioned overnight at 450 K under helium flow and the methanol to dimethyl ether conversion was then tested in the range 450–560 K starting from the lower temperature and increasing in steps of 10 K. At each temperature the gas leaving the reactor was sampled and analyzed by on-line gas chromatography (Carlo Erba Fractovap D) equipped with a TCD detector and a HP 3900A integrator. Data were collected only when steady-state reaction was established and this was generally obtained a few minutes after isothermal conditions were settled. After the whole temperature range had been explored, the reactor was cooled to

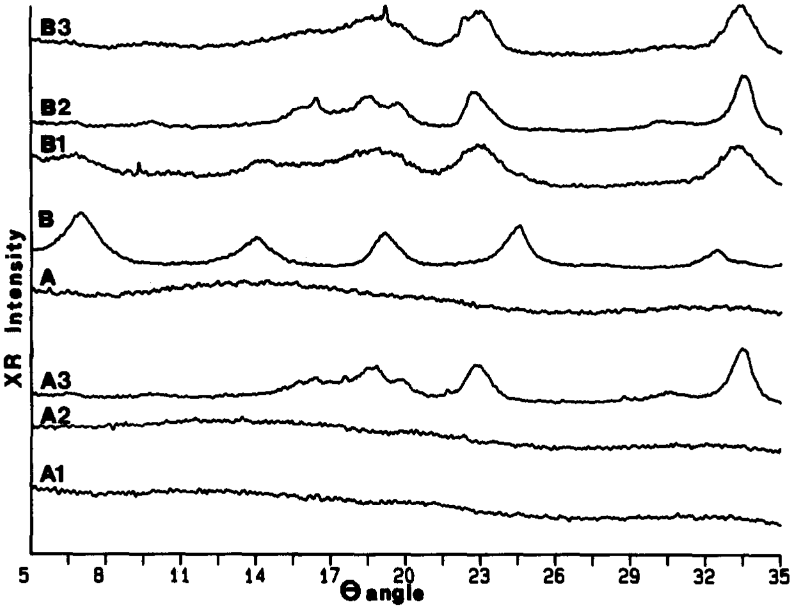

FIG. 1. X-ray diffraction patterns of alumina samples designated in Table 1.

450 K and another cycle was started to investigate whether the catalyst had been modified under the reaction conditions.

From the observed reaction rate and the molecular diffusion coefficient of the gaseous mixture the parameter suggested by Weisz and Hicks (*17*) as an influence index of the transport phenomena was evaluated. The gaseous flow throught the reactor was thus set at 100 ml/min to exclude kinetic control by external film resistance.

RESULTS

a. Characterization

The material obtained by the procedure reported in the experimental section (designated as sample A) was characterized by XRD, DTA, and surface area measurement using BET adsorption isotherms at 77 K. It was conclusively established that it consists of amorphous alumina. DTA showed that on heating, the A sample undergoes two exothermic transitions: the first is to γ-Al_2O_3 (onset temperature 1075 K, maximum peak temperature 1118 K) and the second from γ-Al_2O_3 to α-Al_2O_3 (onset temperature 1360, maximum peak temperature 1408 K). The specific surface area determined after outgassing at 473 K for 15 h was about 310 m^2/g.

The specific surface area of sample B was 370 m^2/g, markedly greater than that of the starting product. Both aluminas (A and B) obtained by procedures reported were submitted to further thermal treatments by heating at 673, 923, and 1173 K for 2 h. The materials obtained, respectively designated as A1, A2, and A3, and B1, B2, and B3, were characterized by surface area measurements and XRD. The results are summarized in Table 1. DTA of sample B material showed two exothermic transitions as with the amorphous material, but at different temperatures. This is characteristic of pseudo-boehmite. The first transition (onset temperature 695 K, maximum peak temperature 798 K) is that from pseudoboehmite to γ-alumina and the second (onset temperature 1367 K, maximum peak temperature 1407 K) the transition to α-alumina.

TABLE 1

Characteristics of the Tested Samples of Alumina

Sample	Thermal treatment[a] (K)	Surface area (m^2/g)	Crystal structure
A		310	Amorphous
A1	673	300	Amorphous
A2	923	225	Amorphous
A3	1173	100	γ-Al_2O_3
B		370	Pseudo-boehmite
B1	673	350	γ-Al_2O_3 + pseudo-boehmite
B2	923	245	γ-Al_2O_3
B3	1173	135	γ-Al_2O_3

[a] All thermal treatments were carried out under an air flow which had been previously bubbled through water at 283 K.

b. Catalytic Behavior in Methanol Dehydration

In the range of temperatures selected for the catalytic dehydration of methanol the reaction products were only water and dimethyl ether. At higher temperatures (about 670 K) there was evidence of formation of low-molecular-weight hydrocarbons. Figure 2 shows the observed methanol conversion at different temperatures for three thermally treated amorphous aluminas. For each catalyst the conversion increases as the reaction temperature increases.

On the basis of the alumina specific sur-

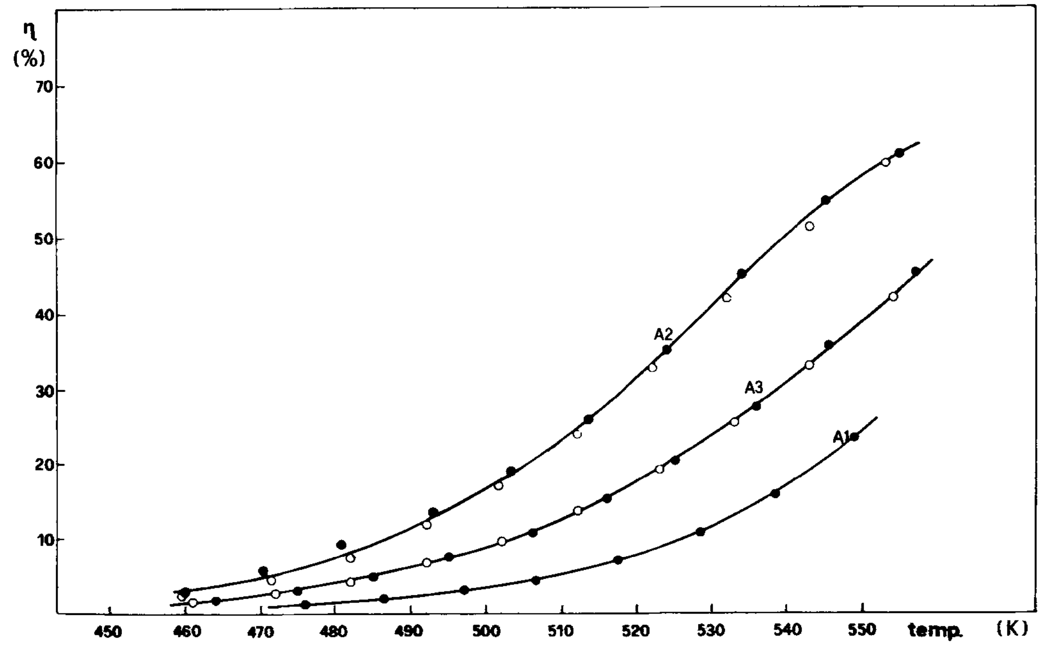

FIG. 2. Methanol conversion versus reaction temperature on amorphous alumina. Catalyst volume, 0.6 ml. Methanol pressure in feed, 23 Torr. Diluent gas, helium. Alumina features as given in Table 1. Open symbols, first run. Solid symbols, second run.

face areas the observed reaction rates at three temperatures are reported in Table 2. These data show that the surface activity follows the same order as the treatment temperature (A3 > A2 > A1) with a marked increase for the A3 alumina.

Higher activities are shown by the catalysts of the B series obtained through hydration of the amorphous alumina samples. The methanol conversion on these materials at different temperatures are reported in Fig. 3. Above ca. 520 K, B1, B2 and B3 show a constant level of conversion in the range 0.65–0.69. This behavior indicates that reaction equilibrium is already approached so that in this temperature range no kinetic data can be used to provide evidence for differences in catalytic activities. This is confirmed by the evaluation of the equilibrium constant for the reaction of methanol dehydration. From 500 to 600 K, according to the thermodynamic data reported by Stull *et al.* (*18*), a theoretical conversion of 0.67 is evaluated, in good agreement with the observed conversion.

Also in Fig. 3 are shown two curves for sample B (i.e., no prior heat treatment). It can be seen that the activity of the catalyst was modified by the reaction conditions of the first run.

TABLE 2

Observed Reaction Rate for Series A and B Aluminas as Catalysts in the Dehydration of Methanol to Dimethyl Ether at 473, 483, and 493 K

Catalyst	Reaction rate (μmol h^{-1} m^{-2})		
	473 K	483 K	493 K
A1	4.36	8.04	11.7
A2	8.34	13.6	18.8
A3	22.4	40.9	59.5
B	1.27	2.06	2.86
B1	29.2	40.0	50.7
B2	63.4	80.9	98.7
B3	35.1	56.3	77.6

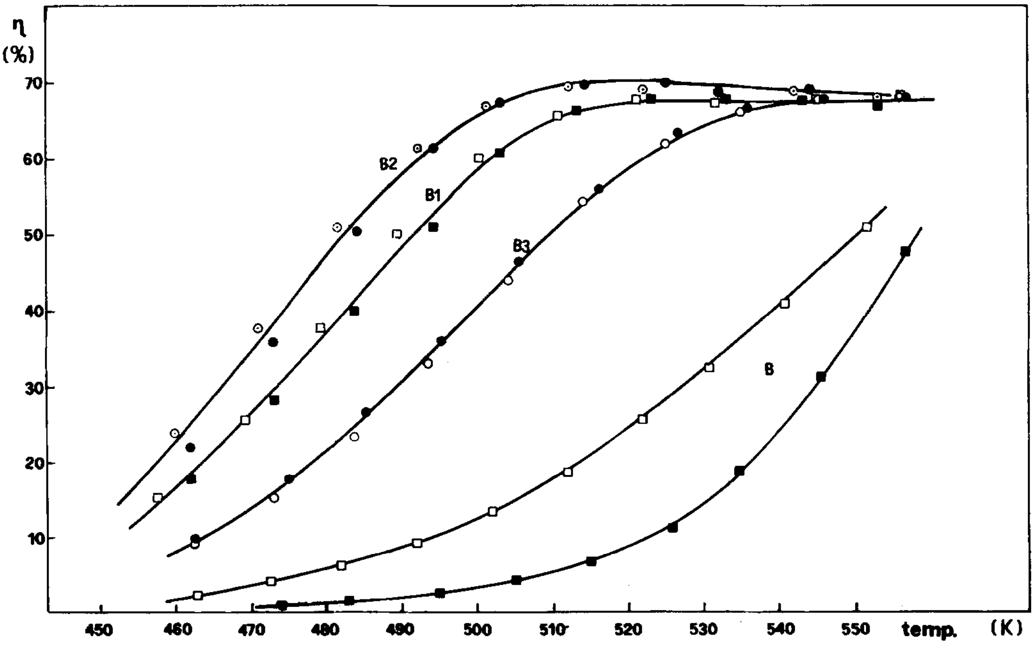

FIG. 3. Methanol conversion versus reaction temperature on hydrated amorphous aluminas. Reaction conditions as in Fig. 2. Alumina features as given in Table 1. Open symbols, first run. Solid symbols, second run.

At the lower temperatures the activity of the aluminas shown in Fig. 3 follows the order B2 > B1 > B3 > B while from the data of Table 2 the activity per unit area is in the order B2 > B3 > B1 > B. In any case there is evidence that the thermal treatment initially causes an enhancement of the catalytic properties of the material despite the simultaneous effect of decreasing the specific surface area. Only by treatment at temperatures higher than 923 K is there a decrease of the catalytic activity.

A sample of commercial alumina (Akzo 001-1.5E extruded γ-alumina of surface area 290 m^2/g) showed a conversion curve between those of B1 and B3 aluminas.

c. FT-IR Characterization

FT-IR experiments have been carried out after activation of samples under dynamic evacuation at temperatures not exceeding those used during preparation (to avoid further bulk transformation). Consequently, activation has been carried out at 673 K for samples A, A1 (spectroscopically equivalent), B, and B1, but at 773 K for all other samples. The spectra show the usual background (cut-off due to bulk Al–O absorptions below 1000 cm^{-1}, maximum transmittance in the region 1500–1200 cm^{-1}, transmission decrease toward higher frequencies due to light scattering above 1500 cm^{-1}) on which some bands due to impurities are superimposed. These bands are very strong on samples A and A1 (near 1560 and 1300 cm^{-1}, rather broad) and arise from residual tartrate and/or nitrate ions. These bands are much decreased in intensity on all other samples, and are completely absent from samples A3 and B3.

After the activation treatment, bands may be observed in the region 3800–3500 cm^{-1}, due to free surface hydroxy groups. However, for the lowest surface area samples (A3 and B3) the transmittance in this region is very low and does not allow the inspection of such bands. The spectra of the samples A1, A2, B, and B2 are reported in Fig. 4. They may be compared with those of the different alumina forms reported in the literature (*19, 20*). The spectrum of sample B2 (γ-Al_2O_3) shows weak components at 3790 and 3770 cm^{-1}, with more evident bands at 3730 and 3680 cm^{-1}. These bands correspond to those generally observed on transition aluminas as γ, δ, and η phases (*1, 2*). The spectrum of the pseudo-boehmite sample B is similar, but with a lower resolution of the two higher frequency components as well as with a much stronger overall intensity of the ν_{OH} absorption.

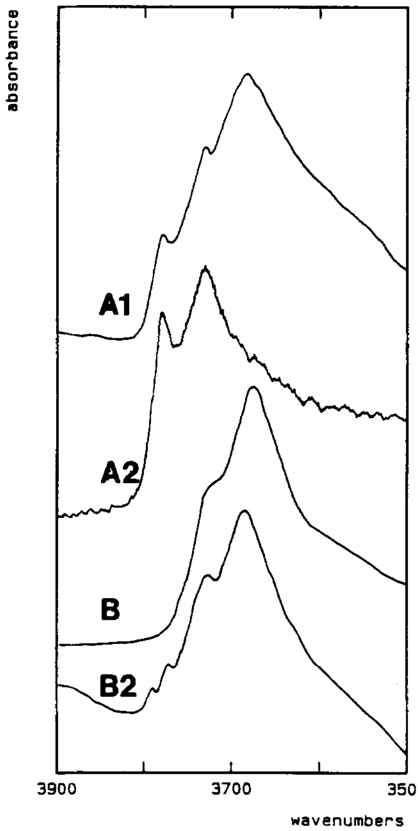

FIG. 4. FT-IR spectra of alumina samples in the ν_{OH} region.

For samples A1 and A2, both amorphous, the spectra are rather different. The spectrum of sample A1 shows again the most intense band at 3685 cm^{-1}, with a shoulder at 3730 cm^{-1}. However, on the higher frequency side a very clear although weak component is evident near 3780 cm^{-1}.

The spectrum of sample A2, rather noisy due to very small light transmittance, shows only well-resolved bands at 3785 and 3730 cm^{-1}.

To characterize further the surface of our alumina samples, we have investigated their Lewis acidity by making an IR study of adsorbed pyridine. The spectra obtained after contact with pyridine vapor and following evacuation at room temperature as well as those recorded after evacuation at 473 K, are reported in Fig. 5 for samples A1, A2, and A3, in Fig. 6 for samples B and B1, and in Fig. 7 for samples B2 and B3. It is known that chemisorbed pyridine undergoes some rearrangement upon heating, resulting in changes in band intensities as well as in frequency shifts. It is also well known that the position and multiplicity of the $\nu 8a$ ring vibration of chemisorbed pyridine (1579 cm^{-1} in the liquid) is related to the strength and number of the different types of Lewis sites.

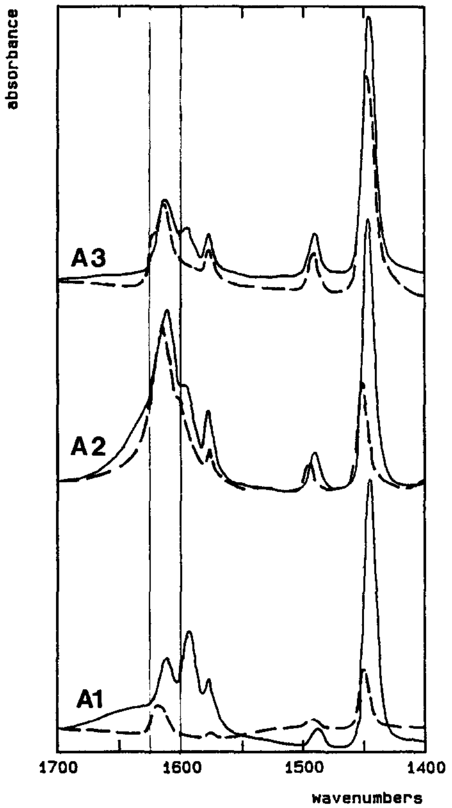

FIG. 5. FT-IR spectra of adsorbed pyridine on series A alumina samples following evacuation at room temperature (full lines) and at 473 K (broken lines).

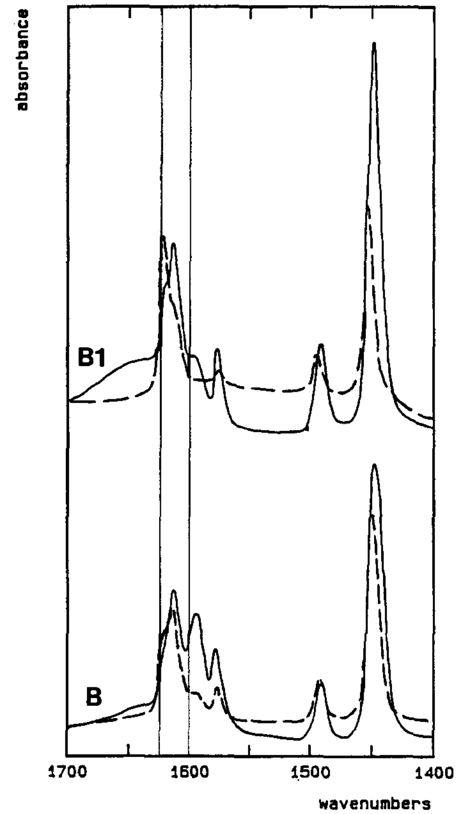

FIG. 6. FT-IR spectra of adsorbed pyridine on samples B and B1 following evacuation at room temperature (full lines) and at 473 K (broken lines).

The spectra of pyridine chemisorbed on the alumina samples may be interpreted, following Morterra *et al.* (*21, 22*), by considering that three types of species are formed, characterized by the $\nu 8a$ band at 1600–1590 cm^{-1} (site III), 1618–1612 cm^{-1} (site II) and 1626–1620 cm^{-1} (site I). From Figs. 5, 6 and 7 it is seen that after evacuation at room temperature the species interacting with sites II and III are clearly evident on all our surfaces. However, the band near 1590 cm^{-1} is more intense on sample A1 than on the other samples. In the samples of the B series, there is also a shoulder corresponding to the ν8a vibration of pyridine on site I. After evacuation at 473 K, the most intense band on the samples of series A corresponds to pyridine adsorbed on site II (near 1615 cm^{-1}), while on samples of series B the intensity of the bands due to species interacting with sites I and II is clearly inverted, except on B itself. We may note that the same conclusions can be drawn if the position and multiplicity of the 19*b* band is taken into account (site I, 1456 cm^{-1}; site II, 1449 cm^{-1}; site III, 1443 cm^{-1}).

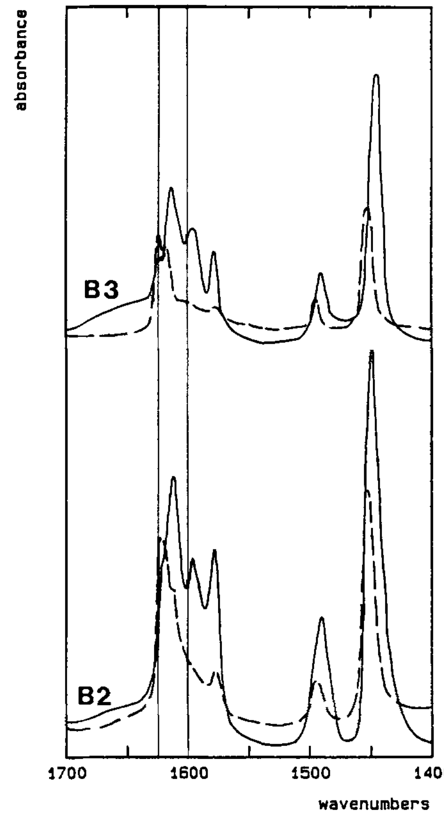

FIG. 7. FTIR spectra of adsorbed pyridine on samples B2 and B3 following evacuation at room temperature (full lines) and at 473 K (broken lines).

DISCUSSION

The data reported above indicate that the decomposition of aluminum nitrate in the presence of an organic reducing agent (in this case tartaric acid) is a useful method for the preparation of high-surface-area aluminas of different crystallinity. Hydrothermal treatments further increase the surface area and favor crystallization; if purely thermal treatments are carried out the amorphous material is stable up to about 1000 K, according to previous data of Teichner and co-workers (*6–8*), and transforms directly to a gamma phase by further heating. The evolution we observe may be schematized as

$$\begin{tikzcd}
\text{amorphous} \arrow[r] \arrow[d, "\text{(hydrothermal treatment)}"] & (1118\text{ K}) \arrow[r] & \text{gamma} \arrow[r] & (1408\text{ K}) \arrow[r] & \text{alpha} \\
\text{pseudo-boehmite} \arrow[r] & (798\text{ K}) \arrow[r] & \text{gamma} \arrow[r] & (1407\text{ K}) \arrow[r] & \text{alpha}
\end{tikzcd}$$

The FT-IR spectra of the samples in the νOH region show that both series A and series B samples are largely hydroxylated after evacuation at 673 or 773 K, as is usual for aluminas. The spectrum of the surface hydroxy groups is similar to the usual one, showing four components near 3790, 3770, 3730, and 3685 cm^{-1} on the B-type samples, while on the A-type samples the first two components are substituted by a single peak near 3780 cm^{-1}. However, the intensity of the components at 3780 and 3730 cm^{-1} seems unusually high on the amorphous sample A2 treated at 925 K.

The FT-IR characterization of the surface cationic sites obtained using pyridine as the probe molecule confirms the existence of three different Lewis sites on the alumina surfaces as observed in the results of Morterra *et al.* (*21, 22*). They interact via a coordination bonding with pyridine, forming three adsorbed species characterized by the $\nu 8a$ band near 1625 cm^{-1} (site I), 1615 cm^{-1} (site II), and 1600–1595 cm^{-1} (site

III). On the samples of series B, as observed by Morterra *et al.* (*21*) for the η form and by Knözinger *et al.* (*23*) for the δ and η forms as a general behavior for the transition aluminas, the three sites are all present. By contrast, on the samples of series A the species interacting with sites I are difficult to reveal, the band at 1625 cm^{-1} being absent or evident only as a weak shoulder. Moreover, on sample A1 the spectrum recorded after evacuation at room temperature indicates an anomalously high concentration of site III (band at 1590 cm^{-1}). Sites I and II have been assigned by Morterra *et al.* (*21, 22*) to coordinatively unsaturated (cus) tetrahedral Al^{3+} and to a pair of cus Al^{3+} ions in octahedral and tetrahedral coordination, respectively, while site III is assigned to cus octahedral Al^{3+} cations.

The presence of the more acidic tetrahedral sites agrees with the high catalytic activity of the B1, B2, and B3 preparations in the methanol dehydration test reaction. This is typical of transition aluminas. It has in fact been shown that a key intermediate in this reaction is the surface methoxy group (*24–26*) produced by dissociation on cus cation–anion pairs having a predominantly acidic character (*25, 26*).

The activity of the amorphous aluminas (A, A1, A2) toward methanol dehydration is much lower, and this is in line with the absence or deficiency of the strongly acidic sites I, assumed to be responsible for the catalytic activity in methanol dehydration. On such samples, the cus octahedral sites III and the cus "mixed" sites II (in the model of Morterra *et al.*) would be in a relatively higher concentration. It seems reasonable to suppose that this reflects the state of the bulk. We therefore conclude that in amorphous alumina Al^{3+} cations are predominantly in an octahedral coordination state. However, the surface appears to transform faster than the bulk toward the structure typical of the transition phases, because of the presence of some sites I and the predominance of sites II on preparations that are still amorphous but have been treated at temperatures nearer to those of the amorphous-to-gamma transformation (A2). Accordingly, sites III, apparently more concentrated on the amorphous samples A and A1, are reported to largely predominate also on α-Al_2O_3 (*22*) and on magnesium aluminate (*27*), where Al^{3+} is in octahedral coordination.

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