

Photoacoustic study of the effect of degassing temperature on thermal diffusivity of hydroxyl loaded alumina

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(Received 19 April 1995; accepted for publication 8 September 1995)

The thermal diffusivity of γ -alumina is determined by the photoacoustic method. The method is calibrated by determining the thermal diffusivity of copper and aluminum. The effect of the chemisorbed hydroxyl groups on thermal diffusivity is studied by degassing the sample at different temperatures. © 1995 American Institute of Physics.

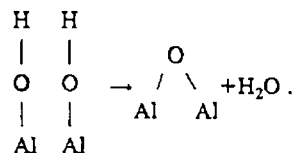
The photoacoustic (PA) effect originally discovered by Alexander Graham Bell in 1880¹⁻⁵ has developed into an elegant, sensitive, and nondestructive method for measuring the optical⁶⁻⁸ and thermal⁹⁻¹¹ properties of materials due to the availability of coherent optical sources and advancement in signal processing and data acquisition systems. The basic principle behind the PA effect is that when a sample is illuminated by an intensity modulated (chopped) light, the resulting periodic optical absorption generates thermal waves and stress in the sample. The PA signal can be detected either directly by using a transducer in contact with the sample¹² or indirectly by keeping the sample in a cell and measuring the acoustic wave generated in the coupling gas with a sensitive microphone. By studying the chopping frequency dependence of the acoustic signal generated in the coupling gas at a fixed optical wavelength, the thermal diffusivity of the sample can be evaluated.¹⁰

Alumina can exist in a wide variety of crystallographic modifications¹³ among which the transition phases η and γ -Al₂O₃ are of special interest in adsorption and catalysis since they can provide high specific surface areas (typically, between 100 and 200 m²/g). These modifications are made up by a defect lattice of the spinel type and can be distinguished by their defect character and the distribution of the cations in tetrahedral and octahedral sites.^{13,14}

The alumina surfaces on exposure to water vapor (moist air) are terminated by a monolayer of hydroxyl (OH) groups. The presence of hydroxyl groups in the surface has been shown by deuterium exchange and infrared spectroscopy¹⁵⁻¹⁷ and by chemical methods. The rehydroxylation of dehydroxylated alumina surfaces on exposure to water vapor is accompanied by a strong heat evolution^{18,19} indicating the strong chemical interaction between surface and water molecule.

On degassing the surface of γ -Al₂O₃ at 650 °C, Peri and Hannan¹⁵ have observed three resolved OH stretching bands at 3698, 3737, and 3795 cm⁻¹; these bands are assigned as "isolated" noninteracting OH groups. Additional bands at 3733 and 3780 cm⁻¹ are also observed by Peri.¹⁶ When de-

gassed below 504 °C broad unresolved bands due to the mutual interaction of hydroxyl groups, are obtained in the OH stretching region. At higher degassing temperatures, the isolated surface OH groups get progressively removed from the surface. After heat treatment at 800 °C, only about 2% of the total hydroxyl content remains on the surface.¹⁶ The removal of OH groups from the surface was postulated to generate "strained oxide linkages," a reaction that may be depicted as



The condensation of the two neighboring hydroxyl groups leads to the formation of a water molecule that gets expelled from the surface. This process leaves an oxide ion in the outer most surface layer and an exposed incompletely coordinated aluminum ion in the next lower layer. This exposed cation acts as a Lewis acid site. According to the model of Al₂O₃ developed by Peri^{15,16} the dehydroxylation process is simulated by a statistical method. Assuming a random removal of hydroxyl pairs without creation of "defects" (adjacent oxide ions or holes), a regular surface lattice can be maintained up to the stage where about 67% of the hydroxyl monolayer has been removed at 500 °C. Remaining hydroxyls can only be condensed to eliminate water with the creation of defects, which comprise adjacent aluminum and oxide ion. About 90% of hydroxyl content gets eliminated with degassing at 670 °C. When heated to 900–1000 °C the hydroxyl groups on the surface gets expelled completely and leaves a coordinated O²⁻ on the outer surface layer.

The single beam PA spectrometer assembled for the present investigation is shown in Fig. 1. The 488 nm line of an argon ion laser (LiCONIX 5300) has been used as the pump source. To generate acoustic signals in the PA cell, the pump beam is modulated using an electromechanical chopper. The PA cell used is a cylindrical, small volume, nonresonant cell made out of aluminum. The cell has an axial bore of about 0.5 cm diameter. One side of the bore is closed by a glass window and to the other side we place the sample and

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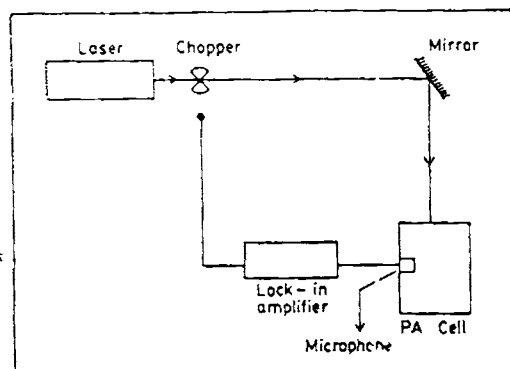


FIG. 1. Single beam PA spectrometer.

the cavity is closed tightly. To detect the acoustic signal generated in the coupling medium, a small, highly sensitive microphone is kept close to the sample compartment in a separate port. The microphone output is processed by means of a lock-in amplifier (EG & G, model 5208).

The PA technique is an effective periodic heat flow method in determining thermal parameters. Here, the PA signal is measured as a function of chopping frequency. Charpentier *et al.*¹⁰ have presented a frequency analysis of the PA signal for the determination of thermal diffusivity. For a given sample thickness, one can have a transition from the thermally thin regime to the thermally thick regime by increasing the chopping frequency, and this appears as a slope change at the characteristic frequency (f_c) in the log (amplitude) versus log (frequency) plot. Knowing the actual thickness of the sample (l_s), the thermal diffusivity (α) can be calculated using the relation $\alpha = l_s^2 f_c$.

γ - Al_2O_3 is prepared by the dehydroxylation of the hydroxous oxides at low temperature ($\sim 350^\circ\text{C}$). The hydroxides are precipitated from the aqueous solution of aluminum nitrate using a 1:1 ammonia solution. The precipitate is washed with water until it is free from nitrate ions. The precipitate is

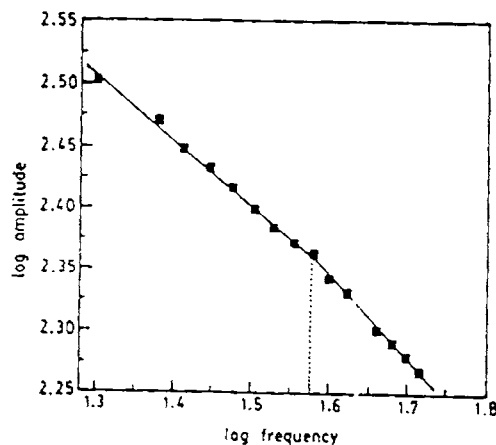


FIG. 2. Log-log plot of the variation of signal amplitude with frequency for alumina at room temperature ($l_s = 1.15$ mm; $f_c = 37.9$ Hz).

TABLE I. Thermal diffusivity of Al_2O_3 degassed at different temperatures.

Temperature °C	Characteristic frequency (Hz)	Thermal diffusivity (α) cm^2/s
30	37.9	0.502 ± 0.001
500	34.8	0.461 ± 0.001
1000	33.3	0.440 ± 0.001

kept in an air over overnight and then calcined at 450°C for 3 h.

To determine the thermal diffusivity, 0.4 g of the sample (with specific surface area^{13,14} roughly of the order of 80 m^2) is pelletized under high pressure. Then the Al_2O_3 sample is kept in an air over at a set temperature for about 3 h in order to degas the sample so as to eliminate the hydroxyl ions. The degassing temperatures selected are 500 and 1000°C since at 500°C about 67% and at 1000°C more than 98% hydroxyl ions will be removed from the sample.^{15,16} Then, keeping the sample in the PA cell, the frequency dependence of the acoustic signal is studied. The log-log plot of the variation of the signal amplitude with frequency for the freshly prepared Al_2O_3 is shown in Fig. 2. Determining the thickness of the sample and the characteristic frequency from the log-log plot, the thermal diffusivity can be calculated using the relation, $\alpha = l_s^2 f_c$. In the present work the sample used has a thickness 1.15 mm and the characteristic frequencies varies with the degassing temperature. The thermal diffusivity of Al_2O_3 degassed at different temperatures is shown in Table I and the values are correct up to the third digit. The accuracy of the measurements depends only on the determination of sample thickness (l_s) and the characteristic frequency (f_c). The thermal diffusivities of copper and aluminum were also determined so as to confirm the validity of the present experimental setup. The values obtained in the case of copper ($1.18 \text{ cm}^2/\text{s}$) and aluminum ($0.979 \text{ cm}^2/\text{s}$) agree well with the reported values ($1.16 \text{ cm}^2/\text{s}$ and $0.98 \text{ cm}^2/\text{s}$, respectively).

From the photoacoustic measurements it is seen that when the sample is degassed at 500°C , α falls by 8.2% of its value before degassing, when it had a monolayer¹⁵⁻¹⁷ of hydroxyl ions. When the sample is degassed further at 1000°C , α falls by 12.2% of its initial value. As described earlier the heating of Al_2O_3 decreases the amount of hydroxyl ions at various sites. The observed decrease in the thermal diffusivity of Al_2O_3 at increasing degassing temperature is, therefore, attributed to the loss of hydroxyl ions from Al_2O_3 .

Table I shows that the value of the characteristic frequency decreases when the sample is degassed at higher temperature. The reason for decrease in thermal diffusivity due to the loss of hydroxyl ion from Al_2O_3 is not clear. Most probably, the creation of defects arising due to the loss of hydroxyl ions may affect the value of thermal diffusivity. Detailed work in this direction is in progress.

In conclusion, the effect of degassing temperature on thermal diffusivity of alumina has been studied using PA effect. The observed decrease in the thermal diffusivity of Al_2O_3 at increasing degassing temperature is, therefore, attributed to the loss of hydroxyl ions from Al_2O_3 .

The authors are thankful to the Department of Science and Technology (Government of India) for financial assistance and one of the authors (SSR) is grateful to the Council of Scientific and Industrial Research (India) for research fellowship.

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