Positron annihilation spectroscopic investigation of Al-pillared montmorillonites

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We report, for the first time, our result on characterisation of Al-pillared clay using positron annihilation spectroscopy (PAS) along with XRD and BET techniques. Positron life-time spectra for Al-pillared montmorillonite, as received and calcined at different temperature (100–500 °C), along with the parent natural clay are measured. The annihilation rate of ortho-positronium (*o*-Ps) increases monotonically with calcination temperature up to 300 °C and falls subsequently. Similar behaviour is seen for the fraction of *o*-Ps formed. We interpret the initial rise in annihilation rate of *o*-Ps to be due to the increase in Brønsted acidity with dehydroxylation of pillars. The reduction in annihilation rate on calcination at higher temperatures could be due to loss of acidity and/or due to mesopore formation following delamination of clay structure.

Keywords: pillared clay, positron annihilation

1. Introduction

Clays [1] are two-dimensional silicates having two basic building blocks, namely, $Si(O,OH)_4$ tetrahedra and $M(O,OH)_6$ octahedra ($M = Al^{3+}, Mg^{2+}, Fe^{2+,3+}$). The sequence of their packing gives rise to different types of clays. For example, when a monolayer of octahedra is sandwiched between two monolayers of Si-tetrahedra, 2 : 1 type of clay minerals are obtained called smectites, and, in the case of Al-octahedra, it is known as montmorillonite. These two-dimensional structures can be made three-dimensional by intercalating the clay with organic molecules or inorganic polycations [2]. This results in increase in the fraction of internal surface area available for adsorption and eventually for catalysis processes like in zeolites. Inorganic pillaring agents such as aluminium hydroxy oligomer or tetrameric hydroxy zirconium ions provide better thermal stability compared to organic molecules. In addition to providing microporosity and thermal stability, the intercalating inorganic polycations are believed to play an important role in catalytic processes by providing acidity to the material. The pillared clays provide an interesting alternative to zeolites in catalytic processes and have attracted considerable attention in basic research. A number of techniques such as XRD, NMR, IR and adsorption techniques have been used and valuable information on its structure, site occupancy and substitutions, acidity, porosity and surface area, etc., are obtained [3].

In recent years, positron annihilation spectroscopy has emerged as an *in situ* probe for characterisation of hidden surfaces in porous materials [4–6,8]. When a positron is injected into a material following thermalisation, it may either annihilate in the bulk or diffuse to the surface and form a quasi-bound species called positronium (Ps). There are two types of Ps, namely, para-Ps (p-Ps) and ortho-Ps (o-Ps). The former is short-lived, with a life-time of 125 ps, and the latter is long-lived (a few nanoseconds) enabling it to interact with the surrounding. The fate of o-Ps, especially its annihilation rate, λ (inverse of life-time, τ), is decided by the void or pore (surrounded by the said surface) size as well as the electron density and consequently the chemical nature of the surface [4]. Since the annihilation rate of Ps is decided by the overlap integral of the Ps wave function and that of the electron on the surface, in case of smaller pore or void the overlap is more and hence the annihilation rate, resulting in shorter life-time, and vice versa. Sensitivity of Ps to the adsorbed gas and consequent modification of the chemical nature of surface as well as to the Brønsted acidity in catalytic materials has been observed [7]. In addition, probability of o-Ps formation measured by its intensity (I_3) is directly related to the surface area of the material [4,8]. In view of this, we have studied natural and Al-pillared clays using PAS with the objective of understanding the positron/Ps behaviour in this material through which its physico-chemical properties can be understood.

2. Experimental

Anhydrous $AlCl_3$ (Spectrochem.) and Na_2CO_3 (S.D. Fine Chem.) were used to prepare 1 M $AlCl_3$ and concentrated Na_2CO_3 solutions, respectively. The latter was added dropwise to the former kept at 90 °C with vigorous stirring. The immediately precipitated $Al(OH)_3$ redissolves by this stirring. The addition was continued till Na : Al was 2.46 : 1. The solution was allowed to cool and age for

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10 days. A series of complex polymerisation reactions take place during this stage ultimately leading to Al_{13}^{7+} polycation [9]. Na-montmorillonite (CEC $\sim$ 7 meq/g) was added to the Al-polycation such that the suspension was 1 wt% and the Al/clay ratio was 4 mg atom Al/g clay ($= 4/13$ mg ion polycation/g clay) and digested at 70 °C for 2 h during which the Na^+–Al-polycation exchange takes place. The intercalated clay was washed with water and alcohol. The product was spread on glass sheet and dried at room temperature. Calcination of these samples was carried out at different temperature from 100 to 500 °C. XRD analysis of the powdered samples was carried out using a diffraction spectrometer (model 1820 Philips diffractometer). The XRD patterns were indexed to obtain a, b and c parameters, wherein a and b refers to clay sheet dimensions and c refers to clay sheet thickness plus the interlayer spacing. The surface area measurement was carried out using the BET technique. All the samples were degassed at 100 °C for 2 h.

Positron life-time measurements were carried out using a fast–fast coincidence spectrometer with a time resolution of 260 ps. The powder samples of natural montmorillonite and its pillared forms calcined at different temperatures, as the case may be, along with the ^{22}Na source were kept in a special cell which was kept under vacuum of 10^{-4} Torr. Stabilisation of the spectrometer was checked in between measurements and data ($>10^6$ counts) were analysed using PATFIT code [10]. Other experimental details are given elsewhere [11].

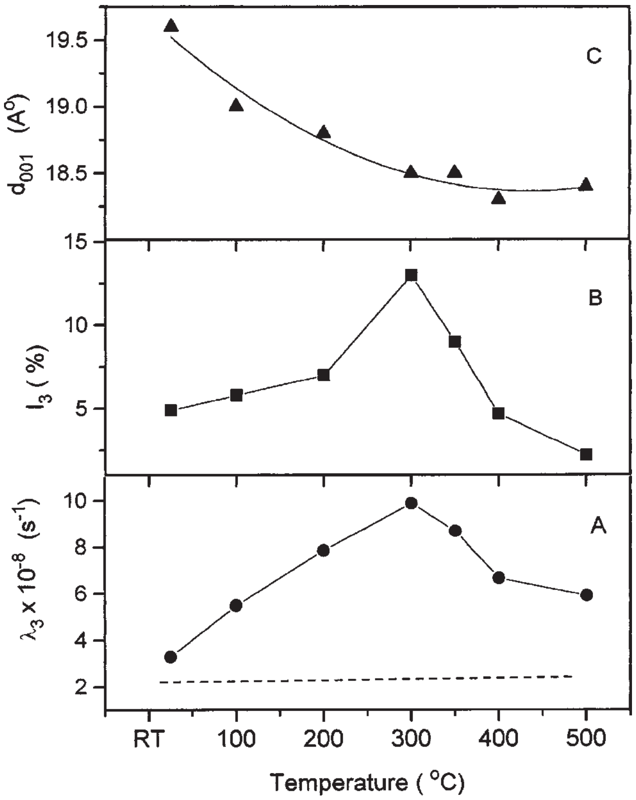

Figure 1. (A) Experimentally observed annihilation rate, λ_3 (solid line) and calculated λ_3 using equation (1) (dashed line) as a function of calcination temperature. (B) o-Ps intensity, I_3, as a function of calcination temperature, and (C) obtained basal spacing (d_{001}) from XRD measurements. Room temperature (RT) referes to as received intercalated sample.

3. Results and discussion

Analysis of life-time spectra resulted in three components ($\chi^2 \leqslant 1.1$); a short-lived component (τ_1) varying from 180 to 210 ps, an intermediate component (τ_2) varying from 450 to 470 ps and a long-lived component (τ_3) varying from 1.01 to 3.04 ns which can be ascribed to p-Ps, free positron and o-Ps states, respectively. The annihilation rate of o-Ps, λ_3 (τ_3^{-1}), its intensity, I_3, along with the measured basal spacing (d_{001}) are shown in figure 1 (A), (B) and (C), respectively. From XRD the obtained d_{001} value of $\sim$19 Å confirms the intercalation of Al_{13}^{7+}-polycation. The surface area of intercalated and calcined samples from BET measurement are seen to vary between 172 and 214 m^2/g as against 52 m^2/g for the natural clay indicating the increase in porosity following intercalation.

It is seen from figure 1(A) that the λ_3 increases monotonically up to 300 °C and then falls rapidly at least upto 500 °C. The basal spacing (d_{001}) is also seen to decrease monotonically with temperature (figure 1(C)) indicating a reduction in the total volume encapsulated by the two layers at higher calcination temperatures similar to the observation reported elsewhere [12]. As mentioned earlier, Ps life-time reduces with the reduction in pore volume and it is tempting to ascribe the increase in λ_3 (decrease in τ_3) to the observed reduction in interlayer spacing with calcination. However, a quantitative estimation of λ_3 for different samples based on interlayer volume points to the contrary, as can be seen in the following section.

From the measured XRD parameters such as a (9.47 Å), b (4.47 Å) and interlayer spacing, i.e., the difference between d_{001} and clay sheet thickness (9.5 Å), the volume encapsulated by two layers of clay was calculated. This in turn can be used to evaluate the expected τ_3 ($1/\lambda_3$) using the universal correlation equation [4]

$$\tau_3 = 7.8\,V + 1.29, \tag{1}$$

where V is volume in nm^3 and τ_3 is given in nanosecond. The resultant λ_3 (τ_3^{-1}) for samples calcined at different temperatures is shown in figure 1(A). It is seen that the change in the expected λ_3 values is very small (from 2.17 to 2.31×10^8 s^{-1}) compared to experimentally observed λ_3 (from 3.28 to 9.9×10^8 s^{-1}). The finite difference between the experimental and theoretical λ_3 values for the as received intercalated sample (referred to as room temperature or RT in figure 1) is due to the pick-off annihilation rate of intercalated pillars. Therefore, increase in λ_3 with calcination temperature cannot be explained using pore volume reduction alone and o-Ps quenching or oxidation reactions seem to be a dominant process. It is known that Brønsted acidity is intrinsic to this material and Ps is oxidised by H^+.

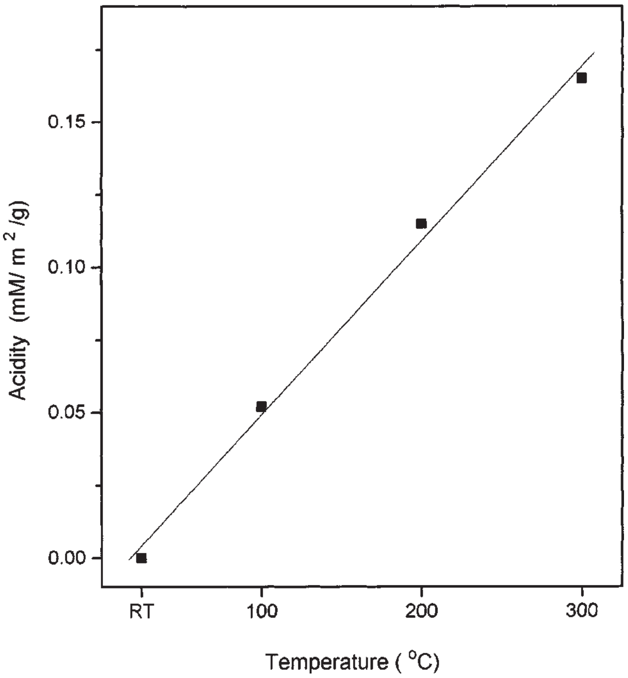

Figure 2. Estimated relative acidities for Al-pillared clay samples at different calcination temperature using equation (3). RT refers to as received intercalated sample.

The reaction scheme for o-Ps quenching can be written as

$$2\gamma \xleftarrow{\lambda_p} \mathrm{Ps} + \mathrm{H}^+ \underset{k_b}{\overset{k_a}{\longleftrightarrow}} \mathrm{Ps{\cdot}H}^+ \xrightarrow{\lambda_c} 2\gamma, \qquad (2)$$

where λ_p = pick-off rate, λ_c = rate constant for Ps with the Ps·H$^+$ complex (quenching rate), k_a, k_b = rate constants for formation and dissociation of Ps·H$^+$ complex,

$$k_{Ps} = (k_a\lambda_c)/(k_b + \lambda_c),$$

where k_{Ps} is rate constant for the reaction between the Ps and H$^+$ and appears in the equation for annihilation decay rate λ_3 as

$$\lambda_3 = \lambda_p + k_{Ps}[\mathrm{H}^+], \qquad (3)$$

where [H$^+$] is the concentration of acid.

Assuming that the annihilation rate for the freshly intercalated sample is due to pick-off process alone, i.e., $\lambda_3 = \lambda_p$ and $[\mathrm{H}^+] = 0$, one can evaluate the acidity using equation (3) if k_{Ps} is known. Although k_{Ps} for this reaction in clay is not available in literature, one can take the limiting value ($-2\times10^{10}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$) which is the diffusion-controlled rate (highest limit) [4] to evaluate the relative acidity in the samples studied. The evaluated relative acidities (at least, the lower limit) from this excercise are shown in figure 2 which indicates that acidity increases with the calcination temperature and reaches a maximum at 300 °C. Our interpretation of λ_3 change (up to 300 °C) to be due to increase in acidity has the following support. First, in the case of a quenching reaction, the I_3 is also expected to increase [6] which is clearly seen in our case (figure 1(B)). Such anti-inhibition of Ps in the presence of Brønsted acidity in metal-dispersed zeolites has also been reported [4]. Second, IR studies [13] have also indicated that Brønsted acidity in Al-PILC vanishes beyond 300 °C, where λ_3 (I_3) are the highest and beyond which there is a steady fall (figure 1 (A) and (B)). Third, the natural clay is known to have acidity [1] due to H_2O in the hydration sphere of the interlayer cation (Na$^+$ in the present case) which is expected to be higher than that in freshly intercalated (Al) sample. The measured λ_3 in natural clay ($9.6 \times 10^8\,\mathrm{s}^{-1}$) is indeed seen to be higher compared to the latter ($3.28 \times 10^8\,\mathrm{s}^{-1}$) which vindicates our assumption that Ps undergoes an oxidation reaction with H$^+$ present in the material.

An important issue to be addressed in Al-pillared clays is the likely location of the acid sites. This is significant because there are different views on this issue, e.g., Yuan et al. [14] report the layer surface alone while Bodoardo et al. [13] suggest the pillars plus the layer surface to be responsible for providing acidity to this material. Our studies indicate increase in acidity with calcination temperature till 300 °C. Since the oxidation of pillars is the important event on calcination, which incidentally contributes H$^+$, we believe that the increase in acidity is primarily due to dehydroxylation of the pillars. Needless to say, there are other sites for Brønsted acidity such as the layer surfaces and edges, but the primary contribution seems to be from the pillars.

On heating beyond 300 °C, λ_3 falls rapidly which can be interpreted as follows. First, it is known that Brønsted acidity vanishes at 300 °C and Lewis acid sites, though stable up to 600–700 °C [13], may not be effective Ps quenchers. Indeed, there is no report on Ps quenching with Lewis acids. Second, there is a possibility of delamination of the clays at higher temperature giving rise to mesopores which are potential trapping sites for Ps. This would cause an increase in τ_3 and, consequently, the λ_3 would decrease, as seen in this work.

In conclusion, we have reported a new result on the characterisation of Al-pillared clays using positron annihilation spectroscopy. Further work on the effect of pillar density on porosity and porosity distribution measurement using CONTIN code [15] is in progress.

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References

[1] R.A. Shoonheydt, in: *Introduction to Zeolite Science and Practice*, eds. H. van Bekkum, E.M. Flanigen and J.C. Jansen (Elsevier, Amsterdam, 1991) ch. 6.

[2] R.M. Barrer, in: *Zeolites and Clay Minearls as Sorbent and Molecular Sieves* (Academic Press, London, 1978) ch. 8;

N. Lahav, U. Shani and J. Shabtai, Clays Clay Miner. 26 (1978) 107; S. Yamanaka and G.W. Brindley, Clays Clay Miner. 27 (1979) 119.

[3] J.R. Butruille and T.J. Pinnavaia, in: *Zeolites and Molecular Sieves*, ed. I.E. Wachs (Manning, 1992) ch. 8.

[4] K.L. Chang and Y.C. Jean, in: *Positron and Positronium Chemistry*, eds. D.M. Schrader and Y.C. Jean (Elsevier, Amsterdam, 1988) ch. 9.

[5] J. Lahtinen and A. Vehanen, Catal. Lett. 8 (1991) 67.

[6] H. Nakanishi and Y. Ujihira, J. Phys. Chem. 86 (1982) 4446.

[7] Y. Ito and T. Takano, Appl. Phys. A 45 (1988) 193;
W.F. Huang, R. Ochoa and R. Miranda, Phys. Lett. A 158 (1991) 417;
W.F. Huang and D.C. Huang, Appl. Phys. Lett. 63 (1993) 1334.

[8] P.K. Pujari, T. Datta and V. Krishnan, in: *Catalysis – Modern Trend*, eds. N.M. Gupta and D.K. Chakrabarty (Narosa, 1995) p. 424.

[9] G. Johansson, G. Lundgren, L.G. Sillen and R. Soderquist, Acta Chem. Scand. 14 (1960) 769.

[10] P. Kirkegaard, M. Eldrup, O.E. Mogensen and N. Pedersen, Comput. Phys. Commun. 23 (1981) 307; PATFIT88 (1989 version).

[11] P.K. Pujari, T. Datta, K. Madangopal and J. Singh, Phys. Rev. B 47 (1993) 11677.

[12] S. Yamanaka, T. Doi, S. Sako and M. Hattori, Mat. Res. Bull. 19 (1984) 161.

[13] S. Bodoardo, F. Figueras and E. Garrone, J. Catal. 147 (1994) 223.

[14] H.M. Yuan, L. Zhonghui and M. Enze, Catal. Today 2 (1988) 321.

[15] S.W. Provencher, Comput. Phys. Commun. 27 (1982) 229;
R.B. Gregory and Y. Zhu, NIM A 290 (1990) 172.