

Characterization of Surfaces, Environmental Molecules and
Oil Shales by Positron Annihilation

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Abstract

Positronium annihilation lifetime technique has been employed to investigate the physical and chemical properties of surfaces and gas adsorptions on various porous media, such as XAD resins zeolites, and alumina. Positronium lifetimes and formation probabilities vary as a function of adsorbate concentrations. By measuring the positronium chemical reaction rate constant of adsorbate, we are able to obtain useful information about the chemical state and mobility of adsorbed molecules, such as NO₂, SO₂, Ni⁺⁺ and Co⁺⁺ on the surfaces. We found a correlation between the total surface area and positronium formation probabilities in these systems. Applications of positronium annihilation technique to surface analysis, environmental science, and fossil fuels are discussed.

Introduction

The investigation of surface and microvoid properties has become one of the most interesting problem in catalytic, environmental science and fossil fuel research today. Most of catalytic reactions and adsorptions only take place on the surface of porous materials, such as graphites, powders and gel systems, which often form a structure with high surface area. One of the most intriguing problems in chemical research is on the understanding of the surfaces and properties of adsorbates inside these porous media.

Modern surface analytical methods can be broadly categorized as: ex-situ, and in-situ techniques. Most of the existing techniques that have evolved using the conventional probes¹ such as photons, electrons, and ions are ex-situ methods. Each of the ex-situ probes approaches the surfaces of interest from outside the sample, and requires an ultra-high-vacuum ($<10^{-8}$ torr) condition. However, most of real surface applications are under atmosphere pressure. Unfortunately, there are very few good techniques that can be considered in-situ. One of the most significant advantages of in-situ methods is that, they can be used to study practical or "real" systems such as catalysts in fine powder and porous forms, as opposed to the ex-situ probes where the investigation are primarily carried out on single cryostat faces. In catalyst and environmental science research, the current interest is to understand how they work on the atomic scale. The major problem is to identify the active sites where bond breaking and rearrangements take place. The activity and selectivity of a catalyst is determined by the surface structure and composition. Most catalytic systems contain high surface area which have a complicated network of porous structure. Characterization of these complex but practical catalyst systems are not very feasible by using ex-situ probe, since many catalytically significant sites are in the closed pores or inner surfaces. It is therefore evident that a probe, preferably in-situ, and microscopic, to atomic scale, is an ideal surface probe to study the chemisty of catalytic systems.

Positronium annihilation spectroscopy (PAS)² is a new analytical technique which is capable of investigating the microvoid and inner-surface properties of porous materials. The advantages of using PAS are based on two facts. First, positronium (Ps), which consists of a positron (anti-electron) and an electron, will annihilate

at a specific rate which is controlled by the electronic density of systems under study. Gas-solid surfaces are the locations where the electronic densities are relatively low. Ps lifetimes are relatively long because Ps lifetime is inversely proportional to the electronic density. A longer lifetime of Ps annihilation has effectively increased the sensitivity using PAS for chemical analysis. The annihilation photons, whose energies are few-tenths of MeV, can be easily detected by standard nuclear technique. Thus Ps annihilation signals contain the electronic density information of materials under study.

The second advantage is that positron possesses unique surface speciality. Contrary to an electron probe, a positron possesses a negative work function in most of solids, i.e. a positron is preferentially diffused or localized to the surface instead of stayed inside the bulk of solids. Because of the surface speciality and sensitivity of positron, Ps annihilation signals are thus mainly characterized by surface states even in complicated porous materials.

Since the positrons emitted from neutron deficient radioisotopes will be thermalized in the bulk of materials in a few picoseconds, these positrons can finally diffuse into the microvoids or interfacial spaces. These positrons approach the surfaces internally, thus PAS is catalogued as an in-situ method which is rarely available in the surface research today. In this paper, we wish to present a series of results in applying positronium annihilation spectroscopy to chemical analysis (PASCA) for catalytic, environmental and fossil fuel systems.

Experimental:

(1) Positronium Annihilation Spectroscopy

Positronium atoms are formed in most of organic substrates. The detection of positronium annihilation is usually carried out by a positron lifetime method which has been known for a few decade in material science and solid state research. Other PAS techniques, such as Doppler broadening and angular correlation measurements of annihilation photons, offer similar or complementary information of lifetime method. In chemical applications, the positron lifetime method gives chemical reaction rate constants which are particularly fruitful.

The positron lifetime measurements were carried out by a conventional fast-fast coincident method, which monitors the starting signal (1.28 MeV γ -rays) from the positron annihilation in the material studied. The resolution of the spectrometer, which was employed in this study as shown in the schematic diagram of Fig. 1, was found to be 380 ps by measuring the coincident photons from a ^{60}Co source. The obtained lifetime spectra were resolved into a function with a sum of multinegative exponential terms by a computer program-POSITRONFIT EXTENDED with two Gaussian resolution functions. The lifetimes were fitted into three components with a source correction of 5% in Mylars, which support ^{22}Na sources. The 5% source correction was determined from a lifetime result in a sample of nitrobenzene in which the solution completely quenches Ps, thus permitting us to determine the proportion of positrons annihilated in Mylar.

(2) Sample Preparations:

XAD resins are copolymers of styrenedivinyl benzene. They are obtained from Rohm and Haas Co., (Philadelphia, Pa.). They are organic copolymers with varying functiona groups. All the XAD resins were subjected to a Soxhlet

extraction procedure with dichloromethane and methanol, water to remove non-polar and polar organic contaminants from the surfaces respectively. The pore structure of XAD resins is stable under this cycling treatments and the observed lifetime results are reproducible at the end of each cycling treatment. Detailed descriptions of these materials can be found in our previous paper.³

Linde molecular sieve zeolite-Y was obtained from Alfa Chemicals (Danvers, Ma) in the powder form. The zeolite-Y belongs to the faujasite family of crystalline aluminosilicates. Their framework structure consists of alternating silica and alumina tetrahedra. The zeolite-Y powder (in the Na⁺ form) was activated at 400°C for six hours under a vacuum of 10⁻⁶ torr. The zeolite-Y powder in the Na⁺ form was employed as the starting material for preparing metal-ion zeolites (Li⁺, Fe⁺³, Ni⁺², Cu⁺²) by impregnating the metal nitrate solutions.

NO₂ and SO₂ were obtained from Linde Division (Speciality Gases) of Union Carbide Co. (research grade purity). The gases were introduced into a calibrated gas manifold system prior to adsorption on to a solid support in a specially designed sample cell. The adsorption of gases and the positron lifetime measurements were performed at 25°C.

The oil shale⁴ was Green River oil shale from the Mahogany zone of the Piceance Creek Basin near Rifle, Co. The raw material contained about 35 wt% kerogen and 2.3 wt% benzene-extractable bitumen. The particle size was about 150 μm (~100 mesh). The positron experiments were performed at room temperature under He atmosphere for different baking temperature.

Applications of PASCA:

(1) Total Surface Determined by PAS

We have measured the positron lifetimes in six different kinds of resins, namely XAD2, XAD4, XAD7, XAD8, XAD11, and XAD12. We observed three lifetime components in each of these resins, 0.4 nsec, 4.5 ± 1.0 nsec, and a long lifetime > 30 nsec. It is the second and third components that are useful in characterizing the chemical and physical properties of resins. Figure 2 shows a plot of I₃%, i.e. o-Ps component versus surface area of these resins. It is obvious that the o-Ps intensity (I₃) is proportional to the surface area. We found a good linear relationship between I₃ and surface area. I₃ is found to be nearly independent of chemical functionality. The existing results of different high surface area systems: oxides,⁵ graphites,⁶ and silicagel,⁷ fall into the same linear equation:

$$I_3 = 3.0 + 0.033 S \quad (>70 \text{ m}^2/\text{g}) \quad (1)$$

$$I_3 = 0.080 S \quad (<70 \text{ m}^2/\text{g}) \quad (2)$$

where S is the surface area (m²/gm) and I₃ is the observed longest o-Ps component intensity in the media. The accuracy of obtaining S values by the above equations is about 7%.

(2) Adsorption Studies of Environmental Important Molecules

By employing the lifetime technique we have studied the chemical

reactivities of NO₂, SO₂, NO and O₂, Ni⁺⁺, Cu⁺⁺, and Co⁺⁺ in porous media. Two long-lived components ($\tau_2 \sim 5$ nsec, and $\tau_3 > 30$ nsec) have been attributed to positron annihilation on surface and in the microvoids of the media. The observed chemical reactivities between positronium atoms and gas molecules in microvoids are found to be smaller than those reported free gas due to caging effect. The chemical reactivities on the surface between Ps and adsorbed molecules on the surface, which in anionic forms, are reported for the first time and are found higher than those in the microvoids. The chemical reaction rate constant (k) were calculated by using Ps kinetic equation as:

$$\lambda_v = \lambda_v^0 + k_v [M]_v \quad (3)$$

$$\lambda_s = \lambda_s^0 + k_s [M]_s \quad (4)$$

where subscripts v, s, signify o-Ps annihilation rate void and surface respectively. Figures (3) and (4) show plots of the annihilation rates in the voids and the equilibrium pressure of SO₂ (P_E), as well as the annihilation rate on the surface and the ΔP (amount of SO₂ adsorbed). In all the systems, we observe the anti-inhibition effect of the surface component (I₂%). The distinct k_s and k_v values for each molecule are new information for chemical analysis applications.

(3) Preliminary Studies of Oil Shale by PAS

The investigation of the chemical and physical structure of combustible minerals and oil-shales has been attempted by PAS. We have measured the positron lifetime for the Green-River oil shale⁴ as a function of baking temperatures. The result is shown in Fig. 5. The measurements were made at room temperature under He atmosphere in order to avoid any further reactions after baking. In spite of the fact that the chemical constituents in such an oil shale are still not known exactly by conventional means, the lifetime results are very interesting in many respects.

The long-lived o-Ps lifetime (~1.3 nsec) indicates that the shale structure consists of interfacial spaces. The quantitative fraction of these layer spaces equals to 4% as measured by o-Ps component. The decomposition of internal organic compounds takes place at 340°C where o-Ps lifetime starts to increase. The optimal decomposition temperature takes place at 350°C as shown in Fig. 5. The decomposition continues up to the temperature about 450°C. Above 450°C, the shale structure becomes void-like since all organic molecules have escaped. The void concentration of the shale increases from 5% to 20% as the temperature increases from 450°C to 600°C as measured by o-Ps intensity. However, the void size (diameter) decreases as a function of temperature. If we employ the known correlation between the void diameter and the positron lifetime for solid substrates,⁸ we obtain the void size diameter varying from 2.5 Å to 1.2 Å from 450°C to 600°C. More systematic studies of positron lifetime and different oil shales are in the progress in our laboratory.

Acknowledgement

This research is supported by NSF (Jean) of USA and WSEF (Cheng) at University of Missouri-Kansas City.

References

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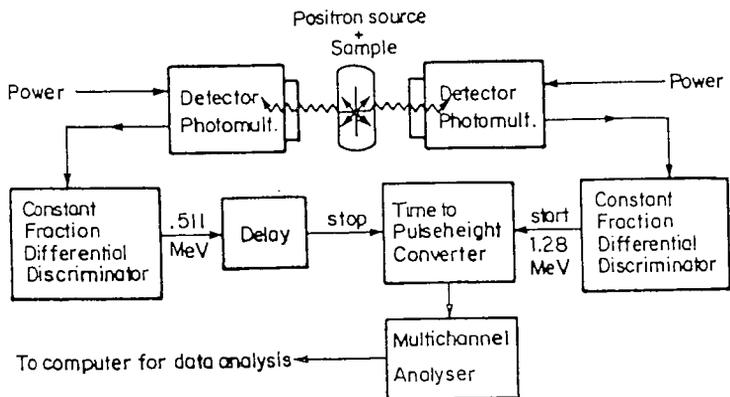


Fig. 1. A schematic diagram for a positron lifetime spectrometer at the University of Missouri-Kansas City.

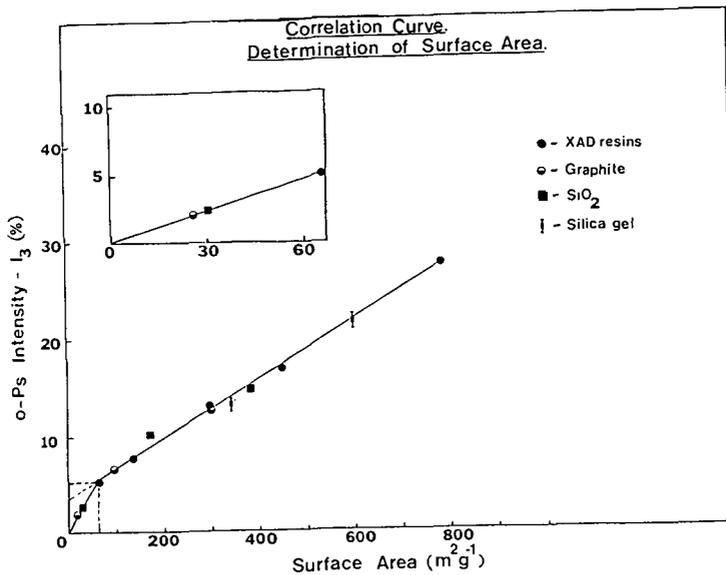


Fig. 2. Plot of o-Ps intensity vs. surface area measured by BET (Ref. 3).

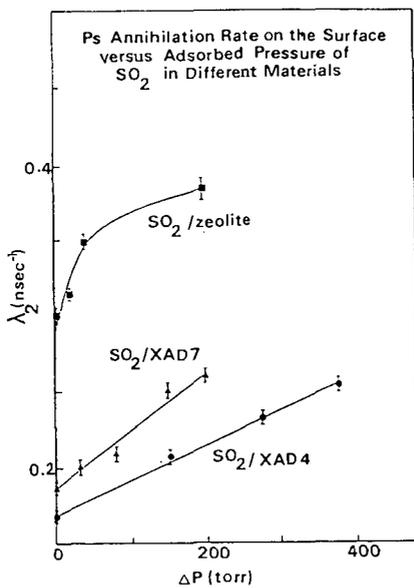


Fig. 3. Plot of the Ps annihilation rate on the surface vs. adsorbed pressure of SO₂.

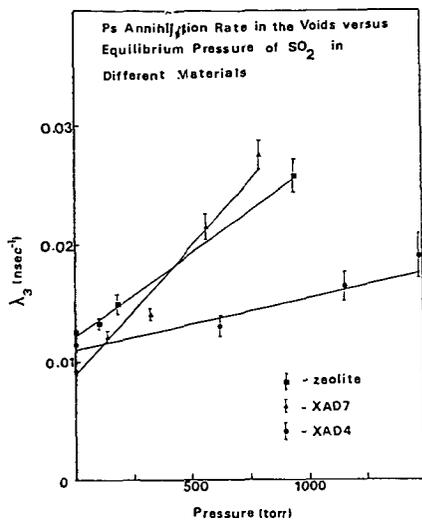


Fig. 4. Plot of the Ps annihilation rate on the surface vs. SO₂ pressure.

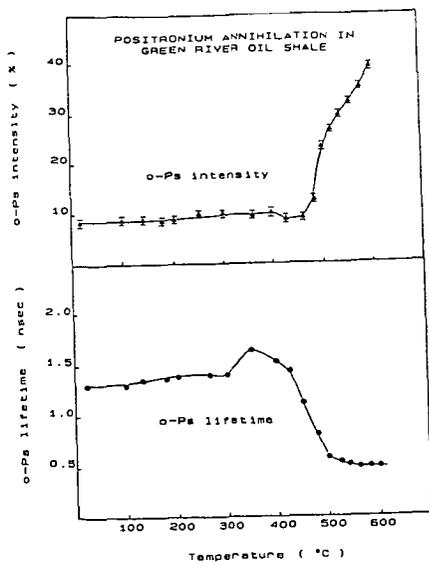


Fig. 5. Plot of the o-Ps lifetime and intensities vs. baking temperature in an oil shale.