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PASCA analysis of Pt–mordenite–Al_2O_3 catalysts

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Positron annihilation spectroscopy for chemical analysis (PASCA) has been applied to differentiate a multicomponent system from the individual constituents. The model catalysts used for this study were a Pt ion exchanged with mordenite and then extruded with Al_2O_3 and Pt impregnated onto a formed mordenite–Al_2O_3 extrudate. Differences were observed between the extrudates and mixed blends of the individual components. This result suggests that the extrusion may modify the location or interaction of the Pt and that PASCA has potential for the characterization of multicomponent catalysts.

Keywords: positron annihilation spectroscopy for chemical analysis (PASCA), mordenite, extrudate, alumina

1. Introduction

In a bifunctional catalyst system, the catalytic behavior for hydrogenation, hydrocracking, or hydroisomerization reactions is determined by the proximity of the metal and acid sites on the support surface as well as by the metal–support interaction. A substantial amount of work has been performed in characterizing the acid center or the metal functionality of either a zeolite or an oxide system. Little work has been performed on a composite system of a zeolite bound by an oxide to form a shaped particle. The purpose of this study was to determine whether positron annihilation spectroscopy for chemical analysis (PASCA) can be used to differentiate a bound or a multicomponent system from the individual constituents.

The PASCA analysis is based on the chemical probes, e^+ (positron) and *o*-Ps (ortho-positronium), one of the bound states of an e^+ and an e^- (electron). The *o*-Ps reacts with surface sites of a solid and annihilates. Positrons annihilate with electrons, which produces two or three quanta of radiation. Those γ-rays carry information about the state of the positron and the electron at the time of their annihilation. Thus changes of *o*-Ps formation probability and *o*-Ps lifetime may provide information with respect to the environment of the surface sites, such as changes of the electron density at the sites as a result of the interaction between metal and its supported material. The annihilation of *o*-Ps can be used to differentiate various surface characteristics. The PASCA analysis has been used to characterize the interaction between the metal and catalyst support [1,2] as well as the acid center [4,5]. For example, this technique has shown that when impregnating Al_2O_3 with $[PtCl_6]^{2-}$ solution, three types of surface sites can be related to the catalytic activity [6].

The objective was to determine whether PASCA could differentiate between differently prepared model Pt–mordenite–alumina composite catalysts. In particular, the purpose of this study was to evaluate whether the Pt that was impregnated onto an extrudate of mordenite–alumina was in a different location than Pt ion exchanged into the mordenite and then extruded with alumina.

2. Experimental

The γ-Al_2O_3 powder was impregnated with varying concentrations of chloroplatinic acid in order to prepare a series of impregnated powders with Pt contents ranging from 0.05 to 0.55 wt%. Varying concentrations of Pt on the H-form mordenite were prepared by ion exchange with $(NH_4)_2PtCl_6$. These ion exchanged powders were then mixed with γ-Al_2O_3 and then extruded. A series of 50% mordenite–50% Al_2O_3 extrudates were impregnated with chloroplatinic acid. All of these materials were calcined and reduced under conditions known to produce well-dispersed Pt.

The PASCA lifetime measurements were performed using a conventional fast–fast coincident technique. Time lag between the starting signal (1.28 MeV γ-rays) from the positron decay in ^{22}Na and the stopping signal (0.51 MeV γ-rays) from the positron annihilation in the sample were monitored and converted into a pulse height signal through the time–pulse height converter. The signal was then passed into a multichannel pulse height analyzer and recorded. Resolution of the instrument was 0.260 ns (10^{-9} s). The lifetime spectra were fitted into three components (τ_1, τ_2, and τ_3) with three intensities (I_1, I_2 and I_3) by using a computer program, POSITRONFIT EXTENDED [7]. The τ_1 values were within 0.105 and 0.125 ns, which could be attributed to the annihilation of *p*-Ps (para-positronium) [8]. The τ_2

values changed from 0.57 to 0.65 ns, which may be related to the annihilation of *o*-Ps in the zeolite cages [9]. The τ_3, which has considerably longer lifetimes, changed from 3.20 to 5.00 ns and may be associated with *o*-Ps annihilation on the external surface of the mordenite or alumina [9]. The τ_3 is the most useful lifetime component in characterizing these catalysts. The review by Miranda et al. [2] provides an excellent overview of the experimental procedures involved.

Analyses were performed on equilibrated samples to make certain that the results were not effected by differences in extent of hydration. Repeat analyses were conducted on several differently prepared samples and at different times. The standard deviation for τ_3 for a Pt-impregnated mordenite–Al_2O_3 extrudate was 0.15 or less than 5%.

Metal content was determined by inductively coupled plasma spectroscopy (ICP). Surface area, micropore volume, and total pore volume were measured with a standard N_2 physisorption technique and calculated using the BET theory of multilayer adsorption to calculate the various parameters. X-ray diffraction (XRD) was utilized to confirm the amount of mordenite in the extrudates. The starting mordenite powder was used as the reference material. Electron microscopy was performed with a dedicated scanning transmission electron microscope (STEM). Samples for the electron microscopy were prepared by grinding the catalyst and then dispersing the finely ground material onto a grid.

3. Results and discussion

The *o*-Ps lifetime τ_3 for Pt impregnated onto the Al_2O_3 powders initially declined and at about 0.10 wt% Pt, increased as shown in figure 1a. A similar trend is noted for the *o*-Ps formation probability (intensity), I_3 (figure 1b). These results are consistent with a strong metal–support interaction existing below about 0.10 wt% Pt content as suggested by Luo et al. [6]. At the higher Pt levels, the site strengths would appear to be fairly similar.

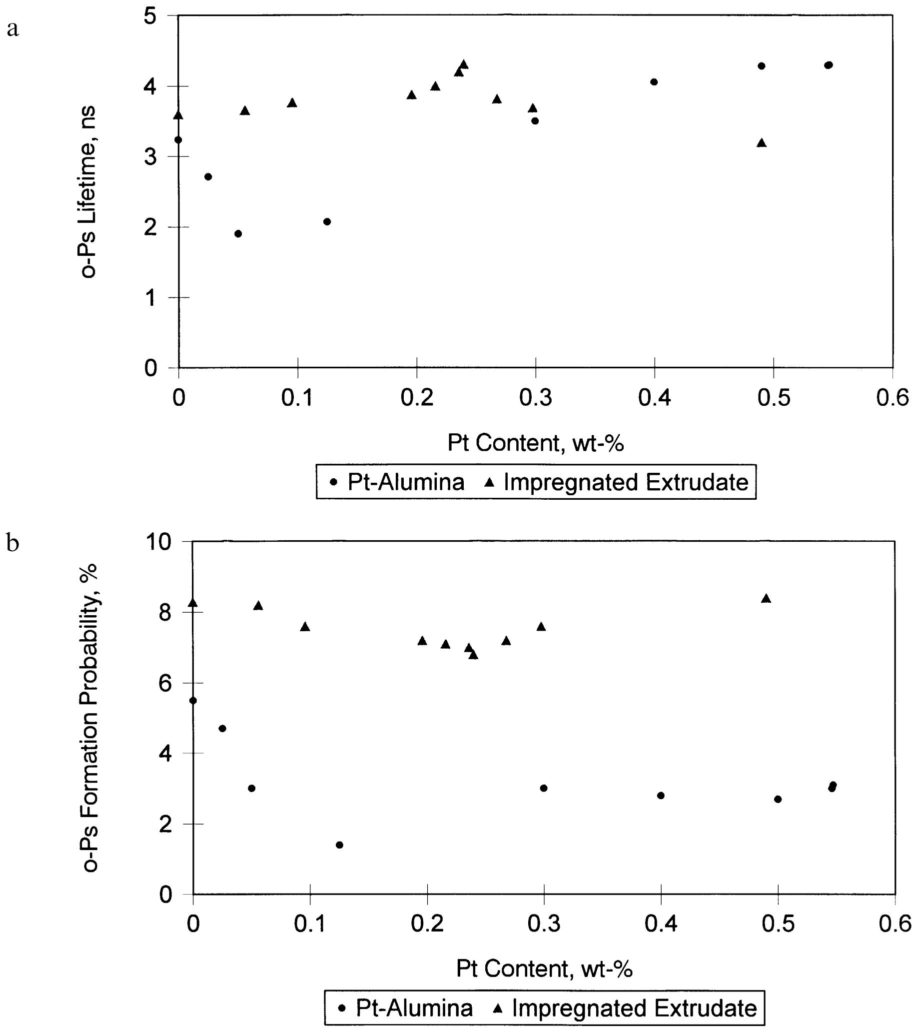

Figure 1. (a) *o*-Ps lifetime and (b) *o*-Ps formation probability as a function of Pt content for Pt impregnated onto Al_2O_3 powder and formed extrudate.

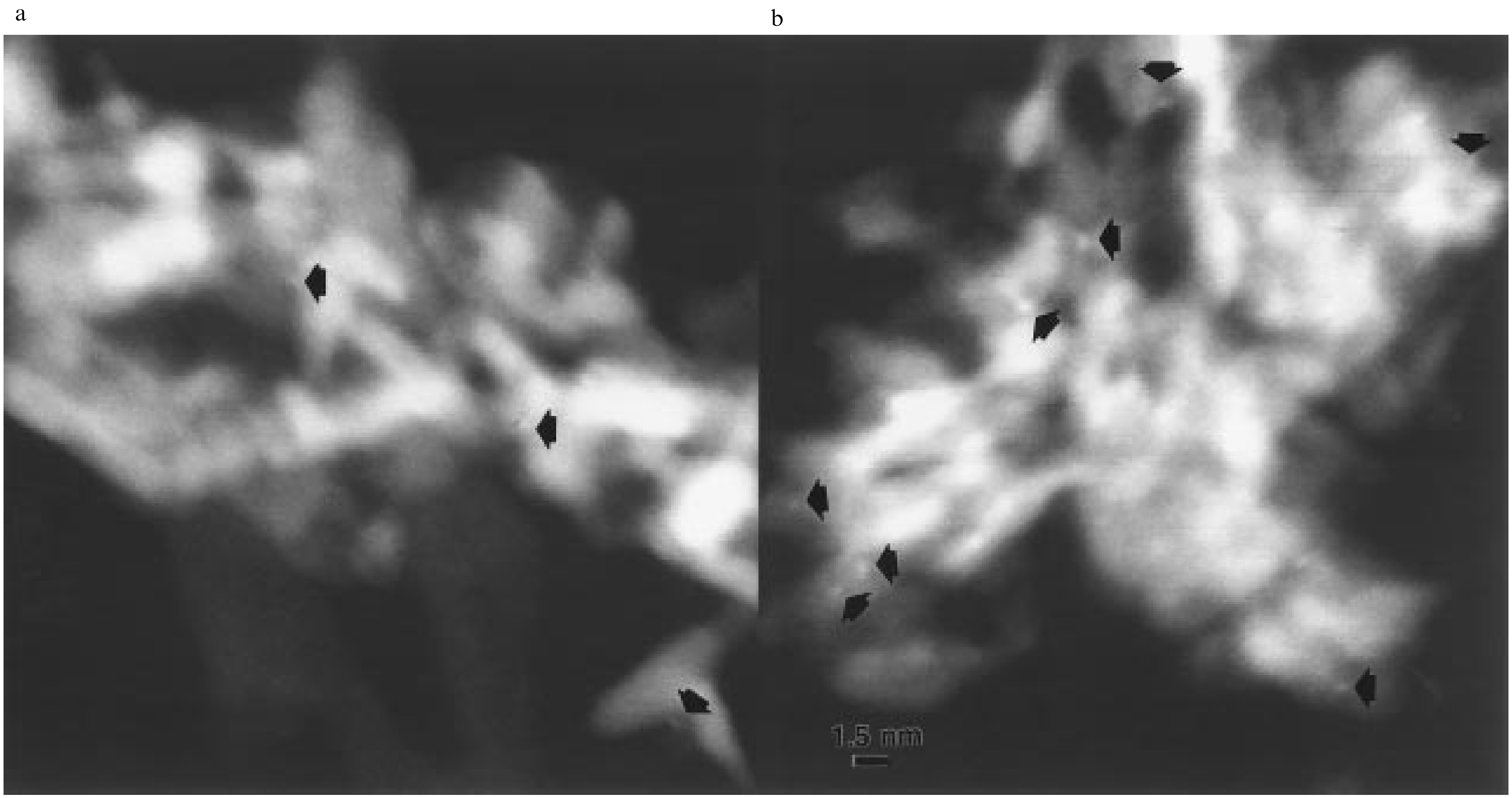

Figure 2. (a) *z*-contrast image of 0.05% Pt on Al_2O_3 showing 0.6 to 0.8 nm Pt clusters. (b) *z*-contast image of 0.3% Pt on Al_2O_3 showing 0.8 to 1 nm Pt clusters.

With the dedicated STEM Pt clusters on a γ-Al_2O_3 support can be imaged by *z*-contrast or high-angle annular dark-field imaging. Using this technique Treacy and Rice [10] have shown that a well dispersed, reduced Pt that has been impregnated onto γ-Al_2O_3 consists of 0.8 to 1.0 nm Pt clusters decorating the catalyst support. For the higher levels of Pt such as 0.3% Pt in this study, 0.8 to 1 nm Pt clusters were observed. However, for the 0.05% Pt impregnated sample the clusters were smaller and ranged in size from 0.6 to 0.8 nm as shown in figure 2. Most were about 0.6 nm in diameter. The initial decline in τ_3 for Pt impregnated onto the Al_2O_3 is probably associated with the smaller Pt cluster size.

All of the extrudates prepared for this study were mixtures of about 50–50 alumina and mordenite and the composition was confirmed by XRD and physisorption *t*-plot or micropore analyses. No Pt crystallites could be found by XRD (less than 3 nm) for any of the extrudates.

For Pt impregnated onto an Al_2O_3–mordenite extrudate, virtually all of the Pt was detected by STEM to be associated with the Al_2O_3. The Pt clusters were only found on the Al_2O_3 binder and these ranged in size from 0.8 to 1.0 nm. Thus for comparison purposes, the Al_2O_3–mordenite extrudate samples can be compared to the analogous Al_2O_3 powder samples that have equivalent Pt contents on the Al_2O_3. When the impregnated extrudates are compared to the powders, some differences are seen in these PASCA results even though virtually all of the Pt is associated with the same component, namely alumina. For example, with the extrudate system the site strengths are virtually the same for all Pt contents. When compared to the Pt impregnated onto Al_2O_3 powder samples, the extrudates are more electron accepting and have a weaker capturing effect at the low Pt concentration. The lifetime τ_3 for the unimpregnated extrudate and powder is more similar than that for the impregnated extrudate and powder. Differences are most pronounced for the low Pt concentration samples and would suggest that the Pt cluster size is the main source for the

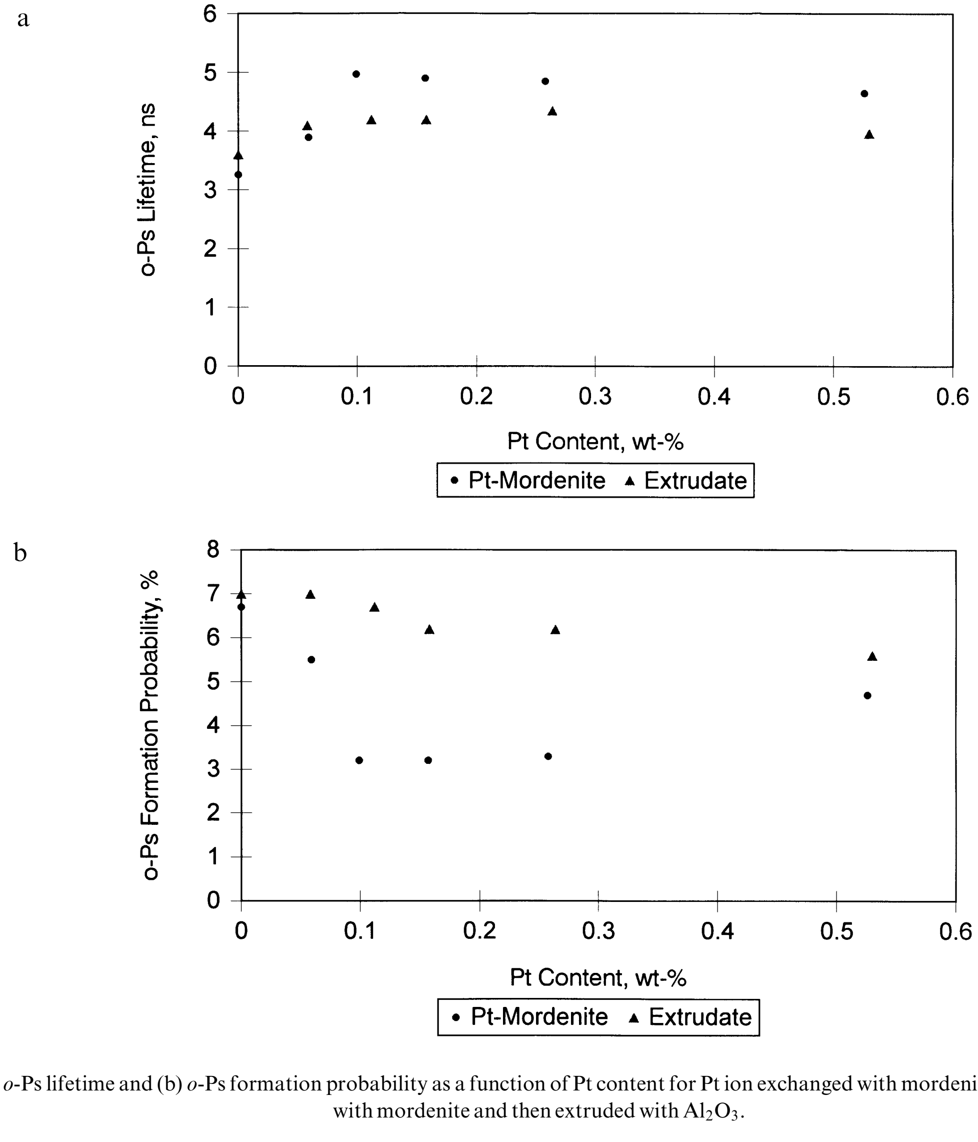

Figure 3. (a) *o*-Ps lifetime and (b) *o*-Ps formation probability as a function of Pt content for Pt ion exchanged with mordenite and Pt ion exchanged with mordenite and then extruded with Al_2O_3.

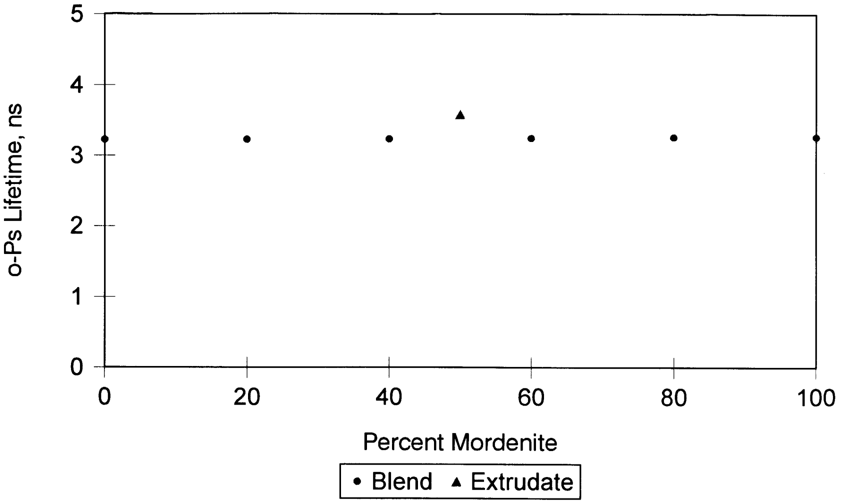

Figure 4. *o*-Ps lifetime is proportionally related to increasing amounts of the individual constituents. The extrudate has a slighly greater *o*-Ps lifetime.

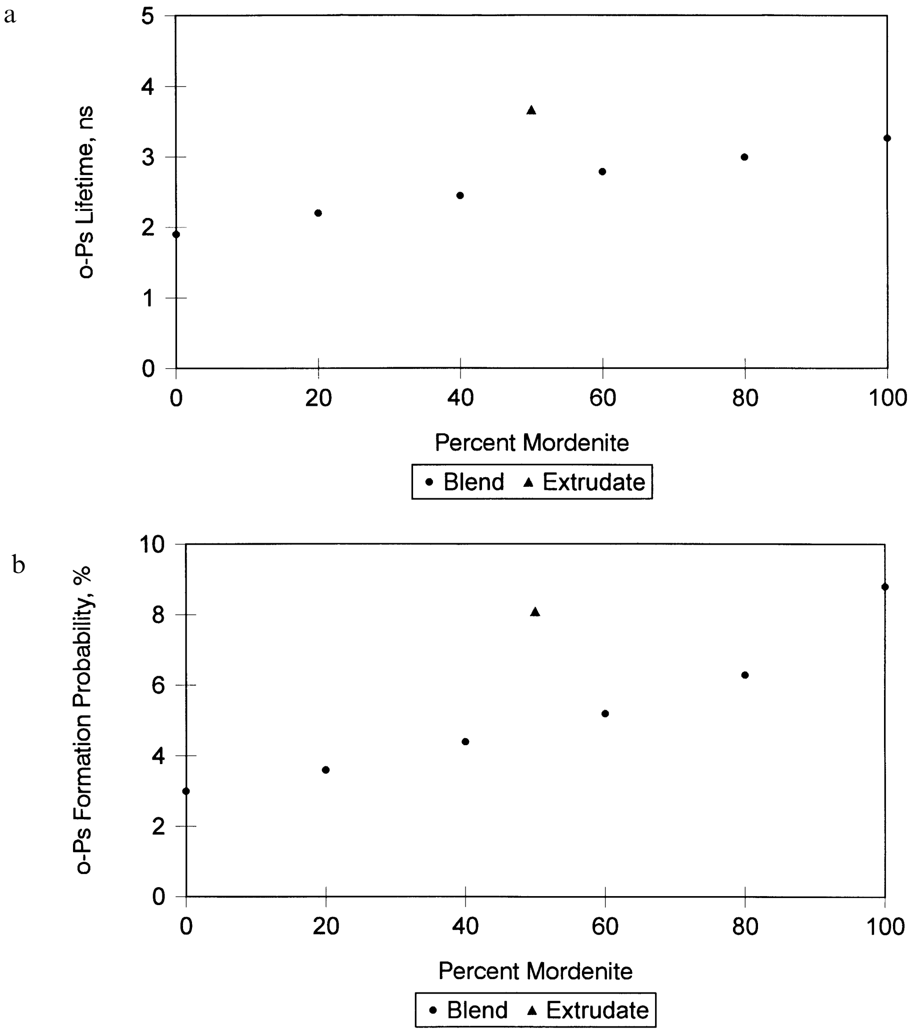

Figure 5. (a) *o*-Ps lifetime and (b) *o*-Ps formation probability being proportional to the amount of the individual components for 0.05% Pt–Al_2O_3 blended with mordenite. A Pt-impregnated extrudate has a greater *o*-Ps lifetime.

difference in τ_3. A higher lifetime τ_2 is observed for the extrudates (0.66 vs. 0.59 ns for 0.25% Pt), which would indicate a greater electron acceptance from the side pockets of the mordenite.

When the sample that was Pt ion exchanged with the mordenite and then extruded with Al_2O_3 was examined by STEM, virtually all of the Pt was found to be with the mordenite. In this particular instance, the ion-exchanged mordenite and subsequently extruded samples can be directly compared to the specific ion-exchanged mordenite that was used to prepare the extrudates. No Pt clusters could be found by STEM indicating that any clusters present are smaller than about 0.5 nm. Although the shape of the τ_3 as a function of Pt contents is fairly similar, the extrudate tends to be more electron accepting for Pt contents greater than 0.075 wt% (figure 3) and would indicate a weaker capturing effect for the extrudate samples. One possible explanation is that the Pt clusters could be of a different size or be in a different location in the mordenite channel such as a pore mouth.

Results from extrudates were compared with analogous powder blends in order to gain further insight. As the concentration of one of the components was altered, the *o*-Ps lifetime, τ_3, and the *o*-Ps formation probability, I_3, changed in a linear mode. The PASCA results for the extrudate samples did not coincide with this linear relationship. The *o*-Ps lifetime for the unimpregnated and extrudate samples were fairly similar. This would indicate that the combined surface area and pore volume were virtually identical for a blend and extrudate [11,12]. An identical conclusion was noted with the N_2 physisorption results. A greater difference in the PASCA results for τ_3 and I_3 were noted for the impregnated samples (figures 4–6), particularly for the Pt impregnated onto the formed extrudate. The extrudate tends to be more electron accepting and has a weaker capturing effect. By using other techniques such as N_2 surface area, XRD, and STEM, these powder blends were indistinguishable from the comparable extrudates. Since the catalyst support prior to impregnation is similar to the

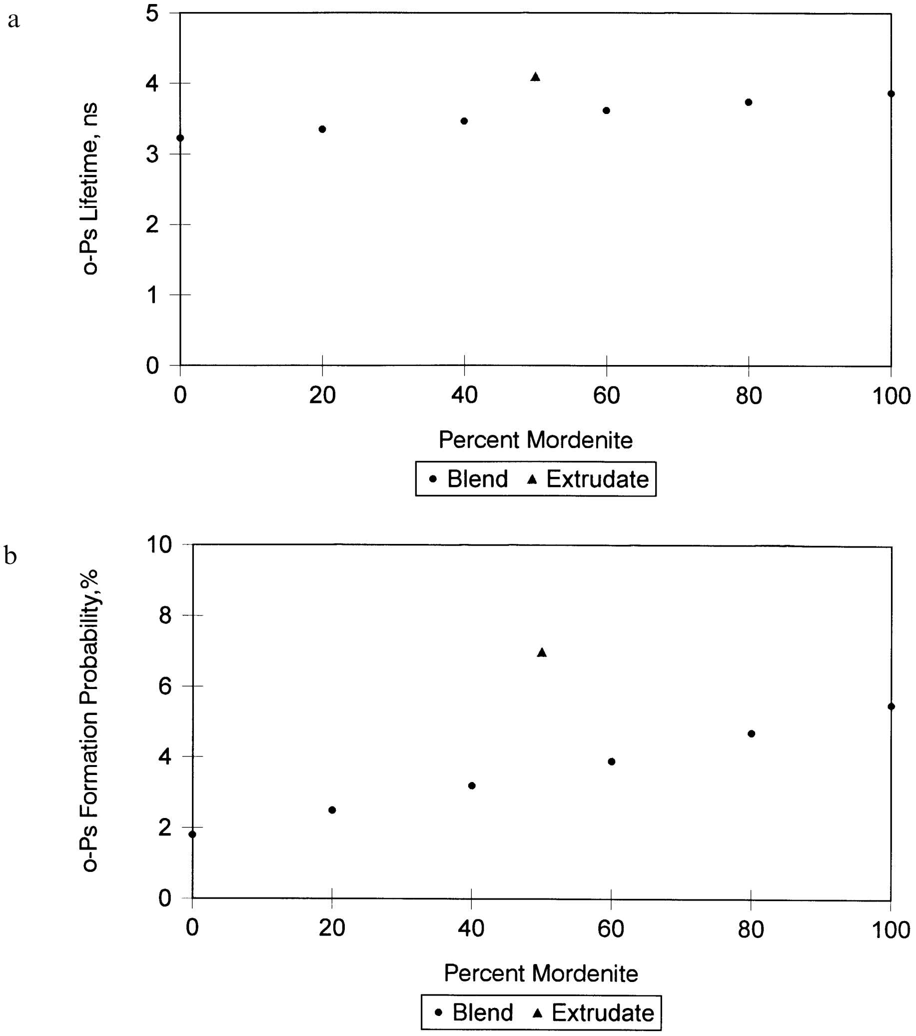

Figure 6. (a) *o*-Ps lifetime and (b) *o*-Ps formation probability being proportional to the amount of the individual components for 0.059% Pt ion exchanged onto mordenite. A Pt-ion exchanged onto mordenite and then extruded has a greater *o*-Ps lifetime.

blended powders, the differences in the PASCA results are most likely attributable to the Pt impregnation. The value of τ_2 seemed to be independent of whether the sample was extruded or not and whether Pt was present. Thus, τ_2 appears to vary solely with the amount of mordenite–alumina and structure of the mordenite–alumina as opposed to the presence or location of Pt. The value of τ_2 is greater for the mordenite than for the alumina, but when mixed together by either blending or extrusion, the resulting value is an average. This is because there are no cages in mordenite for Pt.

Some of the differences in the PASCA results between the extrudates and the analogous powders could be attributed to the extrusion process. However, the greatest differential was observed with the Pt-impregnated extrudates. These results would be consistent for a fraction of the Pt that is associated with the external surface of the mordenite after impregnation. Whether the Pt is present in the channel or pore mouth cannot be ascertained from these analyses. However, a fraction of the Pt in the Pt ion exchanged mordenite and then extruded samples ends up in more electron accepting sites. Thus during extrusion, calcination, or reduction a small amount of Pt may be mobile. Such sites are most likely associated with the mordenite, possibly pore mouths, than with the Al_2O_3 since τ_3 declines when Pt is impregnated onto Al_2O_3. The amount of Pt that is mobile must be quite small as it is below that which can be observed or detected with the STEM. PASCA results can be affected by other factors such as oxidation state, extent of hydration, acid site strength and degree of coordination. However, given that both blends and extrudates were treated similarly, it is difficult to conceive that these could be contributing factors.

Pt mobility in mordenite was found by Lerner et al. [13,14] to occur upon exposure to water vapor of the calcined precursor prior to reduction. They suggested that the Pt migrated to the pore mouths where it was more active for methylcyclopentane conversion.

4. Conclusions

Differences in Pt location were observed depending on whether the Pt was ion exchanged with the mordenite and then extruded with Al_2O_3 or the Pt was impregnated onto a formed extrudate. In the former case, virtually all of the Pt remains with the mordenite, but in the latter situation, virtually all of the Pt is associated with Al_2O_3. The PASCA results indicate that these extrudates are not merely combinations of the individual components as is, for example, the micropore volume. Instead at low Pt levels, the extrudates are more electron accepting than the blend of similar constituents. These results suggest that a small fraction of Pt in the Pt-impregnated, formed extrudate may be interacting with the mordenite. Whether this Pt is associated with the pore mouth cannot be determined from this study. PASCA appears to provide unique insight into catalysts and should become a useful catalyst characterization tool.

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