

Interaction of the Mu-cyclohexadienyl radical with metallic (Au, Pt) nanoparticles in mesoporous silica

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Abstract. μ SR and ALCR techniques have been used to investigate the structure and dynamics of the Mu-cyclohexadienyl radical interacting with Au and Pt metal nanoparticles (MNPs) supported in mesoporous silica (SBA-15). Surprisingly, coherent precession signals are observed and the isotropic hyperfine coupling constants are almost the same in loaded and unloaded samples, implying that the electronic structure of MuC_6H_6 is only weakly perturbed by the presence of the MNPs. We propose the observed radicals are shielded from the metallic surfaces by a benzene coating on the MNPs. The Δ_1 resonance is observable in MNP-loaded samples at higher temperatures than in the unloaded SBA-15. This is attributed to stronger binding of MuC_6H_6 to the benzene coated MNPs.

1. Introduction

In recent years there has been significant interest in the study of metallic nanoparticles (MNPs), which are seen as potential “green” catalysts compared with traditional oxidants in industrial usage. However, it is difficult to monitor and detect chemical reaction products in such a catalytic environment, particularly when free radicals are involved. Muoniated free radicals are relatively easy to study in bulk liquids compared to the protonated versions but the method is typically not useful on surfaces. However, conventional energetic muon beams can be used to probe muonium and its reaction products on surfaces when the specific surface area of the sample is sufficiently large as is the case with MNPs.

The highly reactive MNPs are typically stabilized with protective coatings made of citrates [1] or thiols [2] to prevent their agglomeration. However, for catalysis it is often desirable that the MNPs be uncapped so that guest molecules can bind directly to the MNP surface. In this case the bare MNPs must be supported in inert substrates such as zeolites [3], and silica [4] to prevent agglomeration.



In recent years we have been pursuing the study of muoniated free radicals in faujasitic zeolites [5,6], NaY, HY and USY, which are silica-like substrates that have been used extensively in the petrochemical industry as molecular sieves and heterogeneous catalysts [7]. The USY environment closely resembles that of the present study in mesoporous (SBA-15) silica, both having multi-channel pore structures, although the pore structures in SBA-15 are about ten times larger. This motivated a recent study using mesoporous silica as a reaction substrate [8] and is also one of the main motivations for the present study of MuC_6H_6 interacting with MNPs in mesoporous silica.

2. Sample Preparation

2.1. Bare mesoporous silica synthesis

SBA-15 was chosen for this experiment because of its more stable channel structure compared to other mesoporous silicas. We used a hydro-thermal method developed by Somorjai *et al.* [9]. Typically, 6.25 g Pluronic P-123 polymer surfactant was dissolved in 127 mL of deionized (DI) water and stirred at 40 °C for about 15 min. Then 0.99 mL of 0.5 M NaF, followed by 9.7 mL of tetramethyl orthosilicate (TMOS) as a silica source was added, resulting in a white slurry. After 3 days aging the sample was washed with ethanol, dried at 100 °C for 24 h and calcined in steps of 5 °C /min up to 500 °C for 5 hours to remove any organic template. The final product was 3.0g of white fluffy powder.

2.2. Au and Pt Nanoparticle Synthesis

Both Au and Pt MNPs were synthesized using a citrate method. Typically, 3.0 g of sodium citrate followed by 6.2 g of polyvinyl pyrrolidone (PVP) was added to 2.0 L of previously boiled DI water. In the case of the Au NPs, 197.0 mg of chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) were added. The dark purple colloidal solution was kept boiling for 15 min and then condensed to a 100mL using a rotavapor at 80 C, and then filled into a dialysis bag for 2 days to remove the polymer. Using this method, 6 nm Au NPs (determined from powder XRD) were obtained. For the larger Au NPs (~ 30 nm), the same procedure was followed with minor changes in the order and amounts. The Pt NPs were obtained by the same method, but starting with the Pt salt (Chloroplatinic acid hexahydrate, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), to give sizes of ~ 7 nm (“small”) and 10 nm (“large”).

SBA-15 samples loaded with MNPs were synthesized using the same methods as for the bare SBA-15 samples. Colloidal solutions are mixed with the Pluronic P-123 polymer, followed by a waiting period for nanoparticle-polymer stabilization. About 3 g of purple powder was obtained for the Au NPs, with a similar amount grey powder for the Pt-NP loaded mesoporous silica samples. Both MNP loaded samples had large total surface areas, determined from Brunauer-Emmett-Teller (BET) nitrogen absorption analysis, to be in the range ~ 650 m²/g to 800 m²/g. The average pore size was ~ 10 nm, except for the small (~ 6 nm) Au-loaded samples which had pore sizes of ~ 4 nm.

3. Results and Discussion

3.1. Weak TF- μ SR of Muonium in Unloaded SBA-15 Silica

It is reasonable to expect that muons injected into SBA-15 will form Mu with a high probability and that the Mu will diffuse into the pores on a short time scale, based on previous results on fine silica powders with similar specific surface area (400 m²/g). In that case this behaviour was established by adding paramagnetic O₂, which rapidly depolarizes any Mu reaching the free space between grains via electron spin exchange (SE) collisions [10]. The same technique was applied here and the results are shown in Fig. 1. The top panel shows there is a large amplitude Mu precession signal in a sample that had been baked and pumped to remove oxygen and occluded water. The bottom panel shows that the Mu signal depolarizes rapidly in a sample

that was not baked or pumped to remove O_2 . This confirms that nearly all the Mu in SBA-15 reaches the pores. Note the fitted relaxation rate of the Mu signal in the baked sample $\sim 3 \mu s^{-1}$ is larger than expected from previous studies of Mu interacting with bare silica surfaces [11,12]. More details on the interaction of Mu with silica surfaces are presented in a separate paper at this conference (see M.H. Dehn et al).

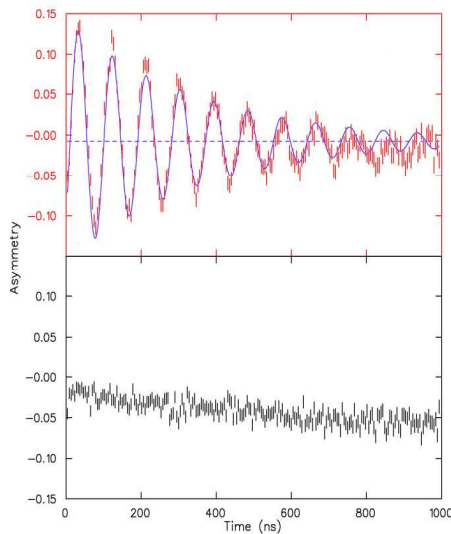


Figure 1. Mu precession in a weak TF of 8 G for the SBA-15 powder baked and pumped overnight (top), compared with the same powder but unbaked and unpumped, thus containing both water and oxygen (bottom). Note the Mu precession signal is completely wiped out. This is attributed to rapid spin exchange of Mu in the pores with O_2 in the gas phase.

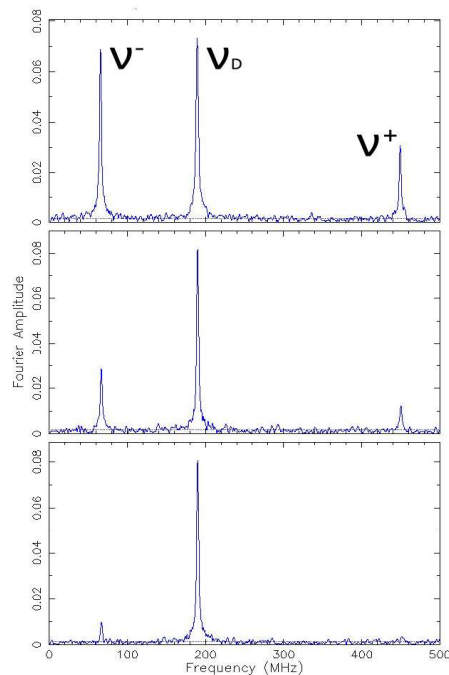


Figure 2. Frequency spectra in pure Bz (top), SBA-15+Bz (middle) and Au loaded SBA-15+Bz (bottom). In all cases the Fourier transform was taken over a time interval from 0.01 to 0.5 microseconds. The relaxation times are all longer than this time so the Fourier amplitude is a good measure of the initial asymmetry. All the spectra were taken at 300K in a magnetic field of 14 kG. The frequencies labeled ν^\pm are from the MuC_6H_6 radical. The large signal labeled ν_D at 190 MHz is due to muons in a diamagnetic environment.

3.2. High Transverse Field μSR of the MuC_6H_6 Radical

The MuC_6H_6 radicals were formed by adding benzene (Bz) from the vapor phase to the bare mesoporous (SBA-15) silica and also to Au and Pt MNP- loaded samples. We expect that the Mu which reaches the pores will quickly add to the benzene to form the MuC_6H_6 radical. This was confirmed by both TF- μSR and ALC studies. The amount of benzene introduced was about 9×10^{-5} moles which is much less than required to cover the silica surface but about 40 times more than required to coat the MNPs with a monolayer. The radical was detected with TF- μSR in a high magnetic field of 12 kG which is sufficient to decouple the muon-electron hyperfine

interaction yielding two well defined muon spin transitions frequencies $\nu^\pm = \gamma_\mu B \pm A_\mu/2$ [13] independent of the spin state of the protons. Typical fourier transforms of the TF- μ SR data are shown in Fig. 2. The top shows pure benzene (Bz) for comparison, the middle is the SBA-15+Bz and the bottom is the Au-loaded SBA-15+Bz. The observed signals originate from radicals which form on a time scale of 100 ps or less, assuming that Mu is the precursor to the observed radical. This can be deduced from the fact that in order for the polarization to be transferred coherently from Mu to MuC_6H_6 the reaction rate λ_r must be faster than the difference in angular frequency between the initial and final state $2\pi(\nu_{\text{Mu}}^\pm - \nu_{\text{Rad}}^\pm)$ [14]. However, the observed radical signal in SBA-15+Bz is less than seen in pure Bz even though the diamagnetic signal amplitudes are about the same. This suggests that some fraction of the Mu in SBA-15+Bz reacts on a slower time scale and therefore does not contribute to the TF- μ SR signal. Finally we note that the signal amplitude in the Au loaded silica+Bz is less than in the bare SBA-15+Bz. It is interesting to note that the ALC spectra (see below) indicate the radical amplitudes are almost the same in the loaded and unloaded samples, consistent with the reduction seen in Fig. 2 being due to a slightly delayed reaction rate, since this would affect the TF- μ SR amplitude but not the ALC spectra.

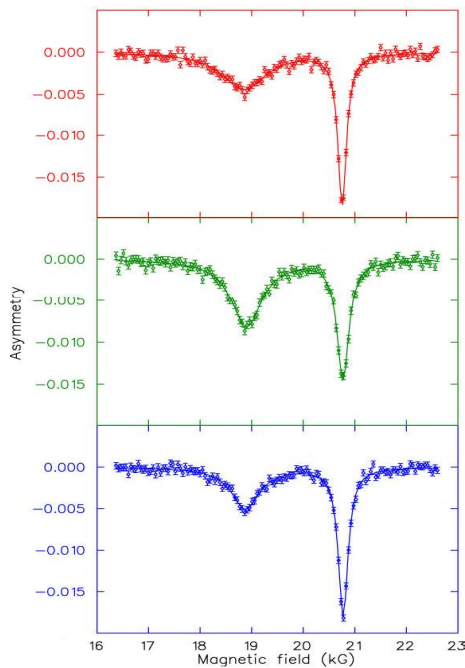


Figure 3. ALC resonance at 323 K for the bare silica (top), the Au-loaded (middle) and the Pt-loaded (bottom). The solid lines are Lorentzian fits

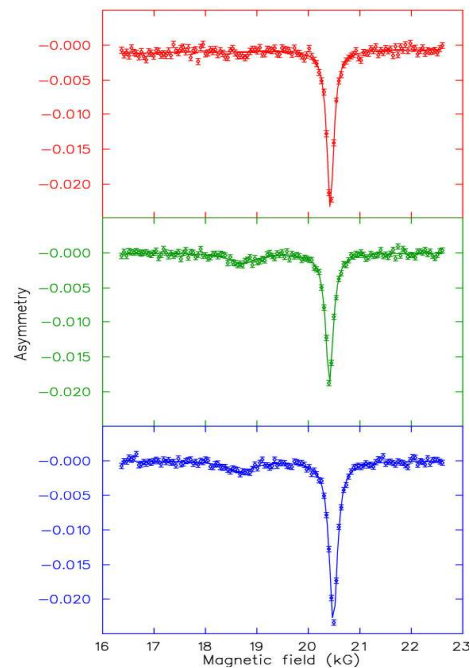


Figure 4. As in Fig. 3 but at 418 K (Pt scan at 398 K). Note that only the Δ_1 resonance for the silica has essentially disappeared into the baseline.

3.3. Avoided Level Crossing Resonance of the MuC_6H_6 Radical

Level crossing resonance or avoided level crossing resonance (ALCR) is a powerful method to investigate electronic structure since it allows one to determine both the muon and all the proton hyperfine constants from the positions of the level-crossing resonances [15,16]. Figs. 3 and 4 shows typical ALC spectra taken on the bare SBA-15 +Bz and the Au and Pt-loaded SBA-15 +Bz. The Δ_0 resonance occurs when the muon transition frequency is matched to

that of the methylene proton next to the muon. Under these conditions there is mixing of the muon-proton-electron hyperfine levels leading to a resonant loss of muon polarization near that particular magnetic field. Note the resonance positions are almost the same in all three samples and shifted only slightly from pure benzene. This confirms the results obtained from TF- μ SR that the electronic structure of MuC_6H_6 in the Au and Pt loaded samples is almost the same as for the unloaded SBA-15+Bz. It is clear the observed radicals cannot be in direct contact with a metallic surface since then one would expect a strong exchange interaction between the unpaired electron of the radical and the metallic electrons, which in turn would have dramatic effects on the structure and electron spin dynamics. This expectation is consistent with the fact that there is no EPR signal for radicals absorbed directly onto a metal surface [17]. In this sense our results are very puzzling. The most likely explanation is that the benzene preferentially coats the MNPs and shields the MuC_6H_6 radicals from direct contact with the metal surfaces. This is reasonable since the amount of benzene introduced was about 40 times that need to coat the MNP surfaces and there is a strong binding energy for multiple Bz layers on metal surfaces [18,19].

Although there are no significant changes in the electronic structure induced by the MNPs, there are differences in the ALC spectra between the Au and Pt loaded SBA-15+Bz and pure SBA-15+Bz which indicate there is some interaction between the MuC_6H_6 and the MNPs. This is most noticeable for the Δ_1 resonances near 19 kG in Figs. 3 and 4. This resonance occurs at a magnetic field where the ν^- transition frequency goes to zero and the applied field exactly cancels the longitudinal component of the muon hyperfine field. This resonance is especially sensitive to the reorientation dynamics of the radical since it is directly sensitive to the muon hyperfine anisotropy (without any influence from the proton-electron hyperfine interactions.) For example in a gas or liquid, or in the pores of mesoporous silica, the Δ_1 resonance is unobservable due to the rapid reorientation dynamics which severely broadens it. On the other hand if the radical is confined to a surface, such that the reorientation dynamics are impeded, this will give rise to transverse hyperfine fields which result in a decrease in the time averaged muon polarization on resonance.

The observation of the Δ_1 resonance implies that the MuC_6H_6 radical is not freely rotating within the SBA-15 nanopores, at least not on a time scale much faster than the inverse of the hyperfine anisotropy [6]. All three samples show similar positions for the Δ_1 (near 19 kG) and Δ_0 (near 21 kG) resonances but the Au and Pt loaded samples exhibit a weaker temperature dependence than the pure silica+Bz sample. In all three samples the Δ_1 resonance broadens and decreases in amplitude as the temperature increases but the effect is more pronounced for the bare silica where it becomes too broad to detect above ~ 350 K. Note also the width of the Δ_0 resonance narrows at high temperature as expected from rapid motion on the surface which averages out any proton and muon hyperfine anisotropy and leads to narrow resonances, similar to that for MuC_6H_6 in liquid benzene. It is evident that the binding energy of the MuC_6H_6 radical to the Bz coated MNPs is greater than the bare silica surface. This can be seen from the spectra shown in Fig. 4, where the amplitude of the Δ_1 resonance in the unloaded SBA-15 is invisible at 418K, whereas in the Bz loaded samples the Δ_1 resonance persists up to this highest measurement.

4. Conclusions

We have used both TF- μ SR and ALCR to study the MuC_6H_6 interacting with surfaces in SBA-15 silica loaded with Au and Pt nanoparticles. Surprisingly, coherent precession signals are observed in Au and Pt loaded SBA-15+Bz. Furthermore the electron structure of the radicals, as determined from the muon and proton hyperfine interactions, are only weakly perturbed by the presence of the Au and Pt nanoparticles. The most significant effect of the nanoparticles is in the dynamics, which suggest that the MuC_6H_6 radical is more strongly bound to surfaces

in SBA-15 loaded with MNP than in the unloaded SBA-15. These results suggest that the observed MuC_6H_6 radical is protected from the bare metal surface of the MNP by several layers of benzene. Additional studies at different loading of Bz and MNPs are in progress which may help understand these intriguing observations. Nevertheless it is already clear that μSR and ALC are unique and powerful methods for investigating the interaction of muonium and of muoniated radicals in these catalytic environments.

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