^{195}Pt MAS NMR Spectroscopy Studies of Pt Containing Polyoxometalates

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Introduction

Pt based catalysts (as polyoxometallates, POM) in fuel cell cathodes, catalytic converters are industrially very important. But due to the chemical inertness of Pt based precursors its synthesis and structural characterizations are very challenging. ^{195}Pt NMR provides an excellent tool for characterizing such compounds since ^{195}Pt chemical shift is very sensitive to the +4 or +2 oxidation states of Pt. However, the large chemical shift anisotropy (CSA) and low natural abundance of ^{195}Pt, makes it very challenging.

Experimental

Pt POM samples were provided by Dr. Kortz and coworkers. ^{195}Pt MAS measurements were done on the 300MHz (^{1}H) spectrometer with a spinning frequency of 14kHz.use of lower field helped in reducing the CSA.

Results and Discussion

Several Pt POMs like $Na_{5.5}[H_{2.5}PtW_6O_{24}]\cdot 17H_2O$(**$H_{2.5}PtW_6$**)[1],$Na_5[H_3PtW_6O_{24}]\cdot 22H_2O$(**$H_3PtW_6$**)[2], $Na_5[H_2PtV_9O_{28}]\cdot 21H_2O$ (**PtV_9**)[3], and $K_7Na_9[Pt^{IV}(O)(H_2O)(PW_9O_{34})_2]\cdot 22H_2O$"("**$Pt(PW_9)_2$**"), using two samples ("**$Pt(PW_9)_2$-A**" and "**$Pt(PW_9)_2$-B**") prepared independently in Korea and from Kortz laboratories were analyzed. A singlet for **$H_{2.5}PtW_6$** and **H_3PtW_6** shows the +4 oxidation state for the Pt ion. The peak width is much narrower for **H_3PtW_6** than for **$H_{2.5}PtW_6$**, reflecting the more symmetrical distribution of protons around the former polyanion. The three peaks for **PtV9** show the presence of two or three well-defined crystal phases of **PtV_9** (e.g. with different degrees of hydration and/or protonation). The absence of Pt in **$Pt(PW_9)_2$** was also confirmed along with its precursor $K_{14}[P_2W_{19}O_{69}(H_2O)]\cdot 24H_2O$**($P_2W_{19}$)**.

Conclusions

High-resolution solid-state ^{195}Pt MAS NMR for POMs is being carried out for the first time and is in excellent agreement with the solution data. Thus this methodology could be easily used to study insoluble Pt-containing compounds.

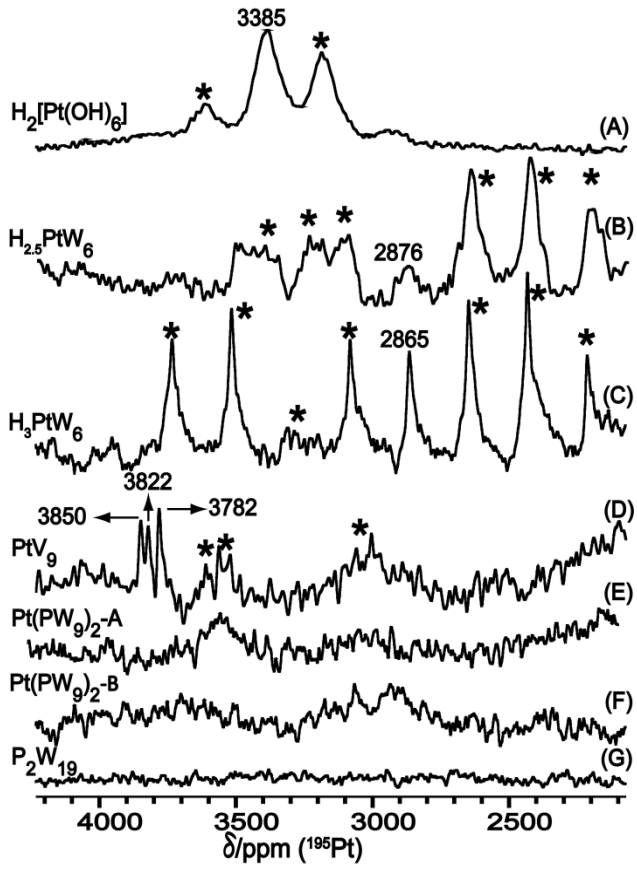

Figure 1. Solid state 195Pt MAS NMR spectra of (A) H2Pt(OH)6 (reference), (B) H2.5PtW6, (C) H3PtW6, (D) PtV9, (E) "Pt(PW9)2-A", (F) "Pt(PW9)2-B" and (G) P2W19 (room temperature), with spinning side bands marked by asterisks.

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References

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