

THE EFFECT OF HYDRATION/DEHYDRATION ON THE AC ELECTRICAL CONDUCTIVITY OF $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ AND $\text{Cs}_4\text{PVMo}_{11}\text{O}_{40}$ USED AS CATALYSTS

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Changes in electrical conductance of $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{Cs}_4\text{PVMo}_{11}\text{O}_{40}$ were studied in dry and humid atmospheres. The electrical conductivity is given by protonic and/or electronic conduction depending on temperature.

Introduction

The attraction for the use in catalysis of heteropolycompounds with Keggin structure in hydration, dehydration, dehydrogenation and oxidative dehydrogenation reactions of organic compound [1÷6] lies in their strong Brönsted acidity combined with redox properties, which can be adjusted by a proper choice of the nature and amount of the constituent elements. These compounds have also other applications as solid electrolytes for fuel cells and in chemical sensing, being sensitive to experimental conditions like relative humidity and temperature.

Electrical properties and acidity of heteropolycompounds depend upon the presence of water in variable amounts. Some of these heteropolycompounds show high protonic conductivity and the adsorption of water enhances in some conditions the electrical conductivity [7÷9].

In our previous papers [8,9] we have used *in situ* AC electrical conductivity measurements to follow hydration/dehydration behavior of heteropolyacid surfaces and of some salts using the change of conductivity response in presence of moisture.

In the present paper a comparison of hydration/dehydration behavior of $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{Cs}_4\text{PVMo}_{11}\text{O}_{40}$ is done by using the same technique.

Experimental

The $\text{Cs}_3\text{PMo}_{12}\text{O}_{40} \cdot 9\text{H}_2\text{O}$ (CsPM) and $\text{Cs}_4\text{PVMo}_{11}\text{O}_{40} \cdot 9\text{H}_2\text{O}$ (CsPVM) samples were prepared from aqueous solutions of the corresponding acids with cesium nitrate added in stoichiometric amounts; the solutions were stirred at 80°C for two hours, then filtered and

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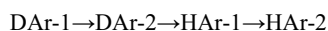
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the solids were dried at 100°C and calcinated at 300°C for two hours in air. Both cesium salts were stable up to 400°C [10].

The specially designed conductivity cell was described previously [11]. The cell is connected to a high precision LRC bridge TESLA BM 484 and to an analytical system (a quadrupole mass spectrometer Leybold, PGA 100 and/or a gas chromatograph provided with TC detector and a column of 1,5 m Porapak) allowing to monitor permanently the composition of the inlet/effluent gas.

The AC electrical conductivity of the samples was measured *in situ* at 1592 Hz at atmospheric pressure between 20°C and 330°C, during linear heating with 2°C/min (by using a differential temperature programmer Chinoin LP 482).

The protocol of experiments consisted of successive heating-cooling cycles performed on the same sample in gas flow; each heating-cooling run was preceded by 30 minute of flushing with the corresponding gas at room temperature. Cycles in dry argon (DAr) and humid argon (HAr) were performed in the following sequence:



The argon used was research grade (99.99 purity). Humid argon containing approx. 2.5 mg of H₂O/l gas was obtained by flushing the gas through a saturator at 25°C.

BET surface area was measured with an surface area analyzer Beta Scientific Corp. 2000 using N₂ adsorption at -196°C, after flushing the samples with a He-N₂ mixture at room temperature followed by heating at 200°C for two hours in helium flow.

Results and Discussion

The surface areas measured for CsPM and CsPVM are listed in Table 1.

Table 1. BET surface areas of CsPM and CsPVM compounds.

Sample	Surface area (m ² .g ⁻¹)
CsPM	138.6
CsPVM	113.3

According to these values, in they belong to the group B of heteropolycompounds² with surface areas between 50 and 200 m².g⁻¹.

The temperature dependences of conductance G for CsPM and CsPVM samples are presented in Fig. 1 (a, b).

On heating in dry argon the G-T plots of CsPM (Fig.1a) show a low temperature (LT) maximum centered at 70°C (the height of which is quite identical in the second run (DAr-2)), and a second maximum centered at about 180°C (the height of the which is smaller, in both cases then the first LT maximum). Above this temperature G decreases up to 240°C, when both curves increase sharply.

A different picture was observed in humid argon-flow. The conductance G decreases from the beginning (30°C) with a shoulder at 70°÷80°C, the minimum being reached at about

230°C. The next run HAR-2 presents a second small minimum at 110°C, then a small maximum at 140°C followed by a decrease of G up to 230°C. After 230°C both curves increase sharply up to 300°C. It must be mentioned that between 230°C and 300°C the increase has a quite similar slope but at slightly smaller G values in comparison with those obtained in dry argon. This can be an indication that similar conduction mechanism occurs in both cases.

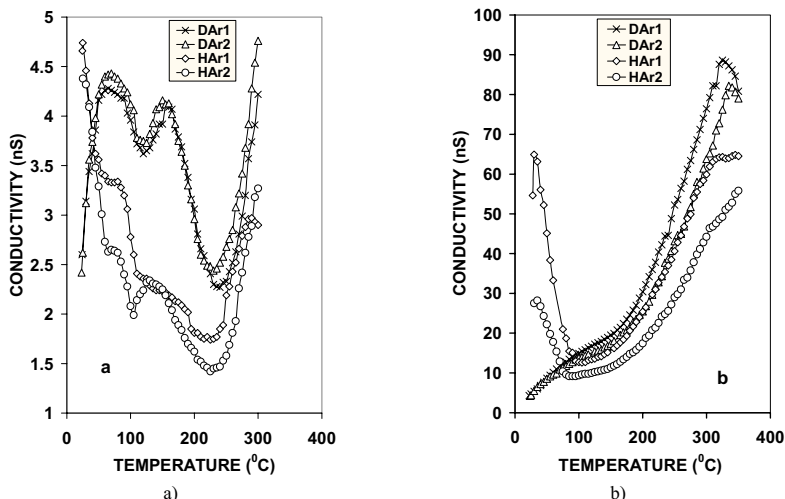


Fig. 1: The variation with temperature of the in situ measured electrical conductance G of the CsPM sample (a) and CsPVM sample (b) during successive flushing with dry and humid argon.

The G temperature plots for CsPVM (Fig. 1b) shows a continuous increasing trend up to 330°C the high temperature (HT) values being higher than the HT values of CsPM. The LT maximum in humid argon, centered at 30°C decreases in the second run. Between 100°C and 200°C the conductance is almost constant, while above 200°C it increases with HT values lower with respect to the previous plots in dry argon.

The activation energies of conduction E_a were calculated from linear increasing sections of the $\ln G$ ($1/T$) plots and are given in Table 2.

Table 2. Activation energies of conduction for CsPM and CsPVM samples in dry and humid argon

Sample	CsPM		CsPMV	
	Temperature range (°C)	E_a (eV)	Temperature range (°C)	E_a (eV)
DAr-1	250-300	0.33±0.03	165-315	0.21±0.02
DAr-2	245-300	0.31±0.03	165-335	0.20±0.03
HAr-1	250-300	0.25±0.01	200-300	0.20±0.01
HAr-2	240-300	0.38±0.04	200-300	0.22±0.01

From Table 2 it can be observed that the activation energies of CsPVM are smaller than those of CsPM. For each sample the activation energies are approximately the same in dry or humid argon. This can be taken as an indication that a similar conduction mechanism occurs in both cases.

The above-presented dependence of conductance G on temperature in dehydrating/hydrating conditions could be explained by the involvement of protonic conductivity [12] at least at low temperatures. Indeed, the measured conductivity σ a compound with two types of carriers is given by:

$$\sigma = \sigma_p + \sigma_e$$

for any combination of positive and negative charge carriers [13], as protons (σ_p) and electrons (σ_e) in our case. Protonic conductivity occurs either by vehicle mechanism (e.g. in presence of mobile molecules of water) or by proton hopping between adjacent proton acceptor sites (at higher temperature) [12]. σ_p decreases with increasing temperature, because the number of carriers (protons and “vehicles”) diminishes due to the water desorption; this is accompanied by the parallel increase of σ_e as a result of thermal activation of electrons and of the increase of the number of donors (anion vacancies). The proportion between the two terms σ_p and σ_e determines the shape of the conductance-temperature plots.

In solid state, the heteropolycompounds are composed of polyanions, protons (and/or other cations) and water. There are two types of water species contained in these structures: crystallization water and constitution water (which is the water considered to be bonded in the form of acidic OH groups). The heteropolycompounds are usually obtained with a large amount of crystallization water. Part of the existing water participates to the formation of what is called “the secondary structure” [1,2], through hydrogen-bonded intermediate $H_5O_2^+$ species. It was shown that most of the crystallization water is removed in the temperature range 20°-95°C [15]. This process is associated in our case with the LT maximum of G-temperature plots in dry argon for CsPM. The second maximum at about 180°C should be connected with desorption of crystallization water more strongly bounded on the surface. DTG-experiments have shown that the crystallization water is removed between 20°C and 170°C for CsPM and CsPVM¹⁵. In the case of CsPVM water is removed continuously in dry argon. The increase of the surface content of water (diffused from the bulk or adsorbed from the gas phase at low temperature) corresponds to the increase of conductivity while the loss of water by desorption results in the decrease of G upon heating. The analysis of the effluent supports the idea that the increase of the conductance plots up to 180°C is associated with the loss of adsorbed species of water, as we have pointed out for other heteropolycompounds [8,9].

In the HT range part of the water remaining on the surface, is supposed to be chemisorbed in anionic vacancies of these compounds. As a result, the high temperature conductivity (dominated by electronic conduction) will be lower in humid ambient in comparison with the conductance in dry ambient.

Conclusions

Our measurements prove that the studied heteropolycompounds have a mixed conductivity, protonic and/or electronic. At low temperature the conductivity is mainly protonic.

The increasing trend observed for conduction above 200°C must be due to the change of the conduction mechanism from mainly protonic to an electronic one.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (AZ436RUM113/13) for financial support and Dr. V. Sasca for providing the samples.

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