

# Evolution of the Electronic Structure of $\text{Cs}_2\text{H}_2\text{PVMo}_{11}\text{O}_{40}$ under the Influence of Propene and Propene/ $\text{O}_2$

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Changes in the electronic and vibrational spectra of  $\text{Cs}_2\text{H}_2\text{PVMo}_{11}\text{O}_{40}$  in the presence of propene (1) or propene/ $\text{O}_2$  (2) were followed by in situ UV/Vis/NIR diffuse reflectance spectroscopy. (1) At 298 K propene leads to reduction as indicated by a broad absorption band extending from the Vis to the NIR range. Iso-propanol was detected at 323 K and the maximum of the broad band shifted from 740 to 700 nm. At higher temperatures the visible absorption band shifted back about 25 nm. (2) Under conditions of catalytic oxidation a propene conversion of ca. 4% was detected with acrolein and CO as major products (670 K). Although the absorption band in the Vis range is less pronounced than in the presence of propene only at the same temperature, the catalyst is not restored to its fully oxidized state. The evolution of a band at 680-700 nm at 620-670 K indicates the formation of a structure with reduced and oxidized metal sites next to each other. This maybe related to the observation of molydenyl and vanadyl species in post mortem Raman spectra.

## 1. Introduction

Cs salts of the vanadomolybdophosphoric acid are, for example, applied as catalysts for oxidative dehydrogenation of isobutyric acid to methacrylic acid [1-3]. The sensitivity of the catalyst under industrial operation suggests that the nature of the active phase may not be identical to the structurally well-defined salts which are molecular solids composed of Keggin ions, Cs cations, and water. Interestingly, the light-off temperature for oxidation reactions coincides with the temperature for the loss of constitutional water [4]. It is thus hypothesized that the water loss is connected to the formation of the active phase, whereby the electronic state of the active phase evolves in an atmosphere that contains both oxidative ( $\text{O}_2$ ) and reductive (hydrocarbon) components at the same time.

In situ UV/Vis/NIR diffuse reflectance spectroscopy offers the unique possibility to simultaneously investigate electronic features such as d-d transitions, intervalence charge transfers (IVCT), and ligand-to-metal charge transfers (LMCT) as well as the vibrational overtones and combination modes of water. From preliminary UV/Vis/NIR experiments, as from other methods (e.g., TG-DTA experiments), it has become clear that catalysts of the type  $\text{Cs}_x\text{H}_4\text{-}_x\text{PVMo}_{11}\text{O}_{40}$  with  $x = 0-2$  are already thermally unstable in the presence of an inert gas. This instability is expressed by the appearance and disappearance of absorption bands.

The goal of this work was to investigate the loss of crystal and subsequently constitutional water, and possible concomitant electronic changes of  $\text{Cs}_2\text{H}_2\text{PVMo}_{11}\text{O}_{40}$  under inert, oxidative, and reductive conditions over a wide temperature range, as well as under the conditions of oxidation catalysis. Propene was selected as a reactant and the gas phase was monitored in order to correlate catalytic performance with spectroscopic data.

## 2. Experimental

A Perkin-Elmer Lambda 9 spectrometer with an enlarged integrating sphere was used for in situ UV/Vis/NIR diffuse reflectance spectroscopy on different dilute catalyst samples. Solutions of  $\text{Cs}_2\text{CO}_3$  and heteropoly acid were used for the preparation of the  $\text{Cs}_2\text{H}_2\text{PVMo}_{11}\text{O}_{40}$  samples. Approximately 110 mg of the catalyst (7-10 wt%) were mixed with  $\text{SiO}_2$  (Heraeus, 0.1-0.4 mm) and placed in a microreactor of in-house design operating under continuous gas flow. Sequential spectroscopic measurements were carried out with a scan speed of 240 nm/min, a slit width of 5.0 nm, and a response time of 0.5 s. Spectralon® was used as a reference. The apparent absorption was evaluated from the diffuse reflectance data using the formula  $1-R_{\text{mixture}}/R_{\text{SiO}_2}$ . The feed mixture was 10 vol-% propene in helium or 10 vol-% propene plus 10 vol-% oxygen in helium with a total gas flow of 71 or 74 ml/min, respectively. The gases were analyzed with two gas chromatographs (Perkin Elmer), equipped with heated automatic gas sampling valves, an FFAP column (Macherey-Nagel) and a packed Carboxen-1000 column using FID and TCD in both GCs.

Series A experiments (10% propene): The temperature was held constant for 2 h at room temperature (RT), and then the temperature was increased at a rate of 1 K/min to 323 K, and spectra were recorded over a period of ca. 5 hours.

Series B experiments (10% propene): The temperature was increased from RT to 323 K and then to 670 K in steps of  $\sim 50$  K (5 K/min heating rate), with a 2 h isothermal period after each step.

Series C experiments (10% propene, 10%  $\text{O}_2$ ): The temperature was increased as in Series B with extended isothermal periods of 9 h at 413 K and 19 hours at 670 K.

## 3. Results

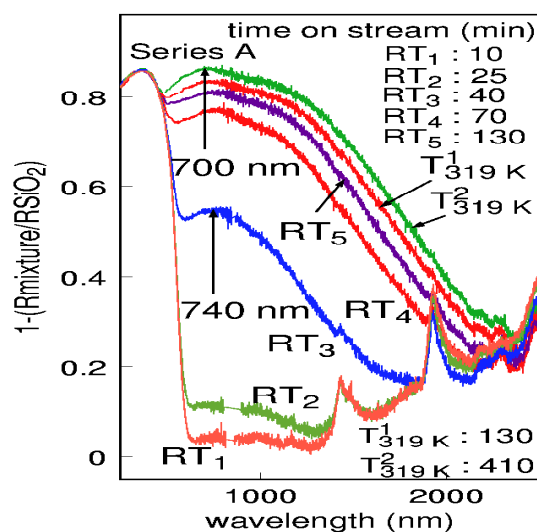


Fig. 1: In situ DR-UV/Vis/NIR spectra of  $\text{Cs}_2\text{H}_2\text{PVMo}_{11}\text{O}_{40}$  at RT and 319 K under the influence of propene.

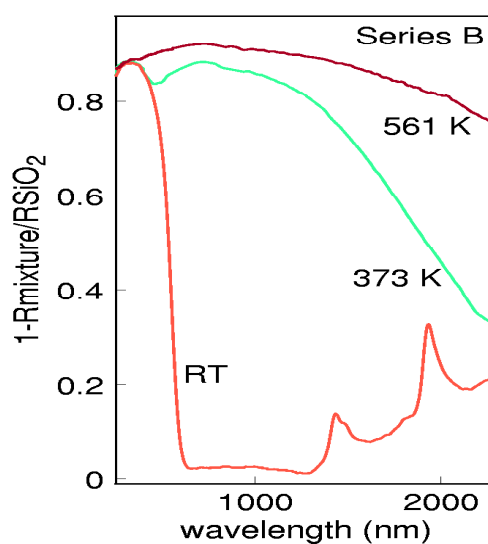


Fig. 2: In situ DR-UV/Vis/NIR spectra of  $\text{Cs}_2\text{H}_2\text{PVMo}_{11}\text{O}_{40}$  at temperatures up to 561 K under the influence of propene.

The Series A spectra show a strong increase in apparent absorption already at RT. After 40 min on stream (RT<sub>3</sub> in Fig. 1) a visible absorption band formed at ~ 740 nm and this band underwent a blue shift to 700 nm when the temperature was increased to 319 K. In contrast to similar experiments using He, the crystal water bands at 1430 and 1925 nm already disappear after 70 min on stream (Figure 1). Formation of iso-propanol was detected at 319 K. Series B spectra showed similarly strong changes in apparent absorption with a red shift of ca. 25 nm for the visible absorption band and the appearance of an additional band in the NIR (at ~ 1050 nm). The NIR band (appearing above 560K) is broad and overlaps with the visible band (Figure 2). The visible band increases with increasing temperature until a single broad visible/NIR band forms. For Series C, increasing temperature leads to a decrease in the intensity of the absorption bands, particularly the NIR band (Figure 3). However, the visible band becomes clearly recognizable again at 563 K; it is possible that a catalytic reaction begins to occur at this temperature. The products acrolein, propionic acid, acrylic acid and water were first detected at 603 K. At 670 K in addition to these products we also detected propionaldehyde, acetone, CO and acetic acid, with the conversion of propene being ca. 4% and that of O<sub>2</sub> ca. 12 %, and the highest selectivities being for acrolein and CO. In the Series C spectra the defined feature in the UV region does not disappear as it did in the Series B spectra at higher temperatures. Under catalytic reaction conditions above 563 K one observes an increase in the intensity of the shifted visible absorption band at 680-700 nm with increasing temperature (=620 K) and time on stream (Figure 4).

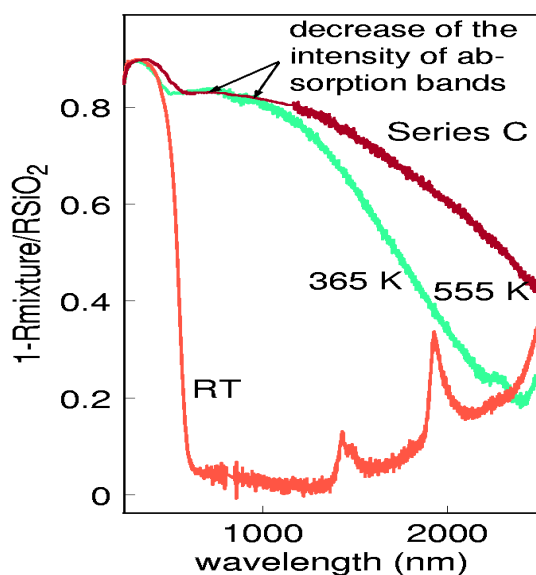


Fig. 3: In situ DR-UV/Vis/NIR spectra of Cs<sub>2</sub>H<sub>2</sub>PVMo<sub>11</sub>O<sub>40</sub> in the presence of propene/O<sub>2</sub>

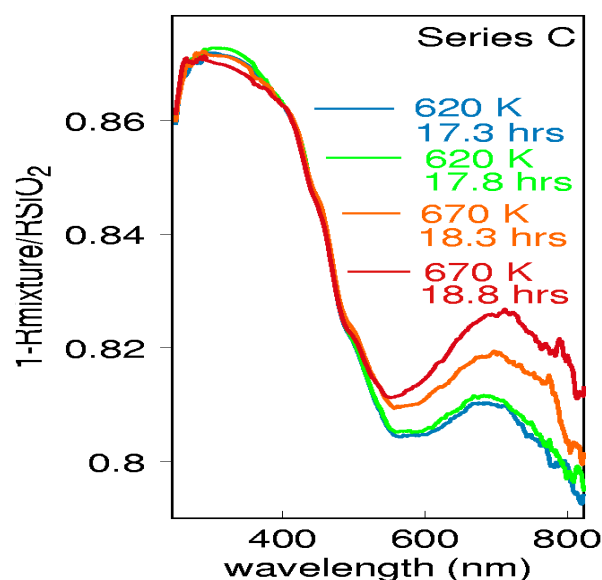


Fig. 4: In situ DR-UV/Vis/NIR spectra of Cs<sub>2</sub>H<sub>2</sub>PVMo<sub>11</sub>O<sub>40</sub> in the presence of propene/O<sub>2</sub>

#### 4. Discussion

The water bands disappear much more readily in the presence of propene than in inert gas, and at the same time, isopropanol is formed. These observations can be explained by an addition of water from the catalyst to propene, a typical acid-catalyzed reaction. Propene thus

appears to draw the crystal water from the catalyst, and when the crystal water is gone the constitutional water is removed as well. The sample apparently underwent considerable reduction even at the relatively low temperature of propene hydration, which corresponds to the observations in inert gas at higher temperature, and reduction generally seems to accompany the water loss. Hence, water, which is added in the industrial oxidation process, may play an essential role in maintaining a certain, i.e. active, state of the catalyst which is different from a van-der-Waals solid built of isolated Keggin units. The electronic structure change in the presence of propene is dramatic; the defined LMCT band is obscured by an intense, almost continuous absorption which is even more pronounced at higher temperatures (up to 670 K). The catalyst sample was black after treatment with the propene atmosphere, in contrast to He-treated catalyst samples that were blue [5].

In the presence of propene and oxygen, the initial reduction at 555 K is partly reversed at 620-670K; however, although excess oxygen is available the catalyst remains in a reduced state. The decrease in the intensity of the visible absorption band below the catalytic reaction temperature (603K) may be attributed to an oxidation of some  $\text{Mo}^{5+}$  and  $\text{V}^{4+}$  centers by the gas phase oxygen. Above this temperature the absorption band increases with rising temperature through the stronger reduction of the catalyst and at the same time the conversion also increases.

The blue shifted absorption band at ca. 680 nm that was observed at 670K could indicate oxygen vacancies that are important for the oxidation reactions. These species may be the same as a species observed in post mortem Raman analysis of these samples that was characterized by a shoulder at about  $1002\text{ cm}^{-1}$  and was interpreted as molybdenyl species [6]. Under the same conditions, the free acid  $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$  showed a blue shift up to 660 nm [5], which might indicate the presence of molybdenyl and vanadyl species in the catalyst sample, since Raman bands were in turn detected at 1008 and  $1030\text{ cm}^{-1}$  [6].

In summary, the changes in electronic structure appear too dramatic to be just a consequence of a partial reduction of the Keggin ion; rather it seems that the geometric structure is partially dissolved leading to a transformation from a molecular solid to more condensed oxidic species with semiconducting character. The availability of relatively free electrons that is suggested by the continuous character of the UV/Vis spectra at high temperatures is a prerequisite for the activation of molecular oxygen and thus for the redox catalytic activity. The structural changes are too severe to allow the restoration of the heteropolyacid through the water that is formed in the propene oxidation; and acidic properties also no longer play a role for the product distribution under these conditions.

## References

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