

## CATALYTIC PROPERTIES OF CESIUM SALTS OF 12-MOLYBDOPHOSPHORIC ACID SUPPORTED ON SBA-15 MESOPOROUS SILICA

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### ABSTRACT

The Cs salt of molybdophosphoric acid  $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$  (CsHPM) was supported on SBA-15 in the concentration of 20, 30 and 40 wt. % loadings. The structure and texture of these CsHPM/SBA-15 composites were studied by XRD, FT-IR and micro-Raman spectroscopy, BET and pore size distribution, SEM-EDS. Thermal stability was investigated by thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The dehydration of ethanol was used to probe the catalytic properties of the CsHPM samples incorporated on the silica matrix. The main reaction products obtained on acid (dehydration) catalytic centres were ethylene and diethyl ether, and respectively acetaldehyde which was obtained on redox (dehydrogenation) catalytic centres.

### INTRODUCTION

Heteropolyacids (HPAs) with Keggin structure and their salts unsupported and supported on different materials may be used for both acid and redox catalysis, as well as in media as heterogeneous (gas–solid and liquid–solid systems) or homogeneous catalysts [1-3]. HPAs are usually impregnated on different porous materials with high surface area (hexagonal mesoporous silica, titania, polymers, molecular sieves) [4-6].

Increasing the amount of surface acidic sites is an important task for the development of useful solid acids applied in different catalyzed reactions. Partial substitution of protons by different cations may result in changes to the number of available surface acidic sites. For example, the salt  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  was reported as superior catalysts which exhibit significantly higher activity than the parent acid in gas phase acid-catalyzed reactions

In order to obtain highly dispersed heteropolyacid species, the Cs salt of molybdophosphoric acid  $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$  (CsHPM) was supported on SBA-15 in the concentration of 20, 30 and 40 wt. % loading. In this work we characterised the texture of these supported HPAs salts in reference to the bulk solid heteropolyacids and investigate their catalytic activity for ethanol conversion.

### MATERIALS and METHODS

The bulk CsHPM with Cs/Keggin unit ratio of 2.5 was prepared from aqueous solutions of  $CsNO_3$  and  $H_3PMo_{12}O_{40}$ . The  $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$  (CsHPM) - SBA15 composites were synthesised as follows: first caesium nitrate was impregnated by aqueous incipient wetness onto SBA-15 molecular sieve, dried and calcined at 300°C and finally 12-molybdophosphoric acid was impregnated by a similar aqueous impregnation route. The CsHPM was deposited in the concentration of 20, 30 and 40 wt. % loadings. Mesoporous silica SBA-15 was synthesized according to the procedure developed by D.Zhao et al. by the hydrolysis of tetraethyl orthosilicate using as surfactant a P123 block copolymer [19, 20]. The texture of CsHPM supported on SBA-15 was studied by SEM-EDX and low temperature nitrogen adsorption technique.

Catalytic conversion and selectivities were measured for vapour phase ethanol dehydration reaction at 250, 275 and 300°C. A differential tubular stainless steel flow reactor,

which was placed into a tubular furnace, was used for the gas phase ethanol dehydration reaction. Before each experiment, 100 mg of the synthesized catalyst was placed in the middle of the stainless steel tubular reactor. Liquid ethanol (99.8% Riedel de Haen) was pumped by a syringe pump at a flow rate of 1.2 ml/h into an evaporator where it is mixed with nitrogen and air to adjust the reactor feed composition. Ethanol was mixed with nitrogen and air at a ratio of Et-OH : N<sub>2</sub> : O<sub>2</sub> = 1:3.5:0.4 in the evaporator. The total flow rate of the vapour stream was kept constant at 30 ml/min.

The composition of the reactor effluent stream was analyzed using a gas chromatograph (Hewlett Packard 5890 GC), which was equipped with a (FID) flame ionization detector. A Poropak QS column was used in the analysis of the product stream. In GC analysis, ethylene, acetaldehyde, ethanol and diethyl - ether peaks were observed at 3.93, 11.75, 12.93 and 15.65 min, respectively. All the connection lines were heated to 150°C to prevent condensation.

## RESULTS

The N<sub>2</sub> adsorption-desorption isotherms of the parent mesoporous silica SBA 15 and CsHPM - SBA15 composites show a typical adsorption curve of type IV as defined by the IUPAC. An obvious hysteresis loop at a relative pressure of  $p/p_0 = 0.4 - 0.9$  is evidenced for the parent mesoporous silica SBA 15 and CsHPM - SBA15 composites.

The specific surface area, pore volume and pore diameter determined from the isotherms using the BJH method are given in Table 1. For parent Cs<sub>2.5</sub>H<sub>0.5</sub>PMo<sub>12</sub>O<sub>40</sub> a narrow hysteresis loop is observed (not shown). The bulk Cs<sub>2.5</sub>H<sub>0.5</sub>PMo<sub>12</sub>O<sub>40</sub> salt displayed surface area of 103 m<sup>2</sup>/g and a pore volume 0.086 cc/g that correspond to the average pore diameter of 34 Å.

The pore size distribution curves of parent mesoporous silica SBA 15 have narrow pore size distribution within mesopore range with a maximum at 62 Å. The pore size distribution curves of CsHPM - SBA15 composites have one maximum within mesopore range at approximately the same values as in the case of pure mesoporous SBA15.

Table 1 Textural properties of Cs<sub>2.5</sub>H<sub>0.5</sub>PMo<sub>12</sub>O<sub>40</sub> - SBA15 composites.

Sample	Specific surface area (m <sup>2</sup> /g)	Pore volume BJH <sub>Des</sub> (cc/g)	Average pore diameter BJH <sub>Des</sub> (nm)
Mesoporous silica SBA15	725	1.19	6.2
20 CsHPM in SBA15	476	0.59	6.1
30 CsHPM in SBA15	445	0.64	6.2
40 CsHPM in SBA15	397	0.47	6.1
CsHPM	103	0.086	3.4

The dehydration of ethanol was used to probe the catalytic properties of the CsHPM samples incorporated on the silica matrix. Catalytic activity of the synthesized CsHPM-silica-based nanocomposite catalysts for vapour phase ethanol dehydration reaction was tested in a fixed bed flow reactor.

The main reaction products obtained on acid (dehydration) catalytic centres were ethylene (ET) and diethyl ether (DEE), and respectively acetaldehyde (ACA) which was obtained on redox (dehydrogenation) catalytic centres. Ethylene and DEE are due to dehydration reactions occurred on the acid sites of the catalyst, while acetaldehyde formation

through a dehydrogenation reaction indicated the presence of basic sites. In the effluent leaving the reactor were detected also unreacted alcohol and minor quantities of CO<sub>x</sub>.

The conversion of ethanol and selectivity were calculated as follows:

$$\text{Conversion} = \text{moles of ethanol reacted} / \text{moles of ethanol in the feed} \times 100 \quad (1)$$

Selectivity was calculated in carbon-based values:

$$\text{Selectivity} = \text{moles of product desired} / \text{moles of reacted ethanol} \times 100 \quad (2)$$

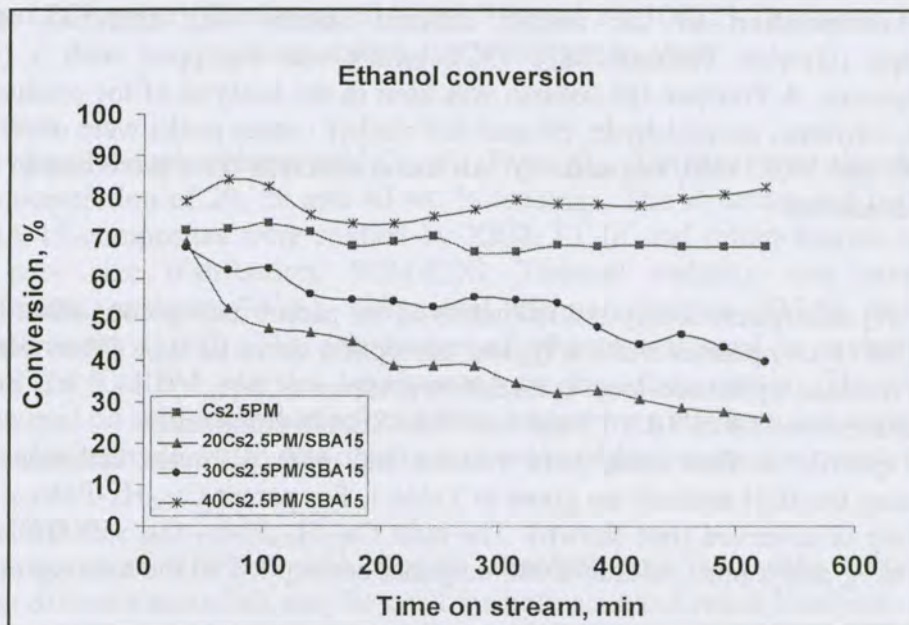


Figure 1 Ethanol conversion values obtained with pure CsHPM and CsHPM - SBA15 composites at 300°C

Ethanol conversion over pure CsHPM and 40CsHPM - SBA15 catalysts has relatively constant values during the time on stream but values of conversion are higher for supported sample. For 20CsHPM - SBA15 and 30CsHPM - SBA15-supported catalysts the values of ethanol conversion are lower in comparison with pure CsHPM ones and a continuing decrease of them with time on stream is evidenced (Figure 1).

The CsHPM-silica-based nanocomposite catalysts synthesized here were found to be very efficient for ethylene formation from ethanol. The highest ethylene yield values were obtained with CsHPM and 40CsHPM - SBA15 catalysts. With these catalysts, selectivity of ethylene has values of around 75 - 85% obtained at reaction temperature of 300 °C. Ethylene selectivity for pure CsHPM and 40CsHPM - SBA15 catalysts has relatively constant values during the time on stream (as in the case of Et-OH conversion) but values of ET selectivity are higher for CsHPM sample. So, after reaction for 500 min, the ethylene yields over 20CsHPM - SBA15 and 30CsHPM - SBA15 at 300°C reached 32% and 58%, respectively.

The DEE selectivity increased with time on stream for 20CsHPM - SBA15 and 30CsHPM - SBA15 -supported catalysts while for pure CsHPM and 40CsHPM - SBA15 catalysts remain nearly constant with the increasing of time on stream. The values of DEE selectivity for 20CsHPM - SBA15 reach the maximum values after 5 h and then remain almost constant.

The third main product obtained in the catalyst test experiments was acetaldehyde. As shown in Fig. 2, acetaldehyde formation was observed in selectivity below 20%. Among the catalysts tested, highest acetaldehyde selectivities were obtained with 20CsHPM - SBA15

catalysts tested at 300 °C. Acetaldehyde (ACA) which is known to be produced on redox centres resulted in significant amount especially on supported catalysts in comparison with pure CsHPAs ones. However, supported 20CsHPM - SBA15 led to higher quantities of ACA, especially after 5 h on stream.

Thus, the very high dispersion of the HPAs on high surface area molecular sieve yielded an active catalyst for ethanol conversion and for acetaldehyde formation. The acetaldehyde selectivity increased gradually with time on stream from 5% to 17% in the case of 20CsHPM - SBA15.

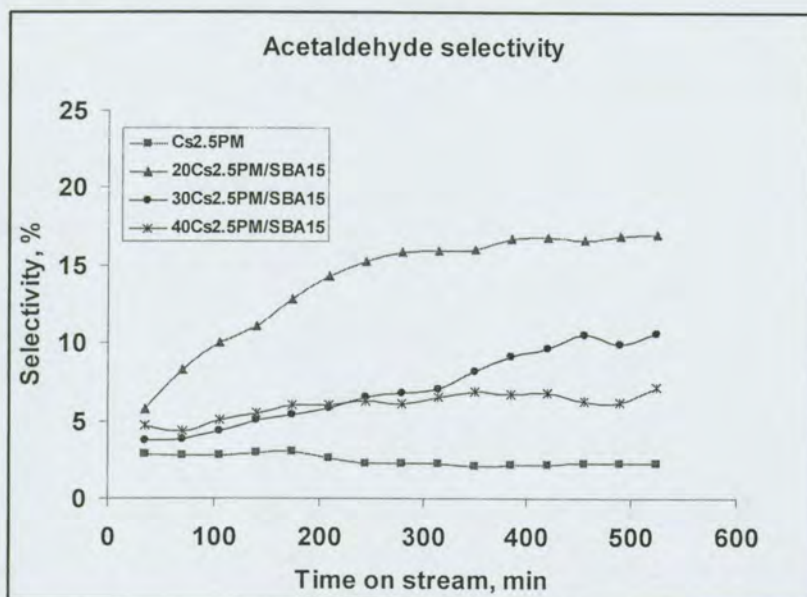


Figure 2 ALAC selectivity versus time on stream for CsHPM and CsHPM - SBA15 composites at 300°C

## CONCLUSIONS

- In this study is described a procedure for supporting insoluble Cs acid salts on mesoporous SBA-15 by two-step sequential impregnation with a variation of active phase content (20-40 wt. %).
- Parent CsHPM and CsHPM - SBA15 composites have showed both acidic and redox properties and therefore the reaction products obtained are ethylene and DEE on acidic centres and acetaldehyde on redox catalytic centres, respectively.
- The favourable effect of CsHPM deposition into the silica pores for oxidehydrogenation pathway to acetaldehyde results from the higher values of ACA selectivity especially for 20CsHPM - SBA15 composites.

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