



# Ethanol to hydrocarbons using silver substituted polyoxometalates: Physicochemical and catalytic study



Mohamed Mokhtar, Sulaiman N. Basahel, Tarek T. Ali\*

Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, 21589 Jeddah, Saudi Arabia

## ARTICLE INFO

### Article history:

Received 6 October 2012

Accepted 20 April 2013

Available online 28 April 2013

### Keywords:

Ag<sub>x</sub>H<sub>3-x</sub>PMo<sub>12</sub>O<sub>40</sub>

Keggin structure

Raman spectroscopy

Acid catalysis

Ethanol dehydration

Ethylene selectivity

## ABSTRACT

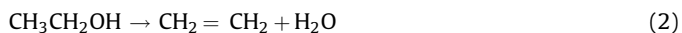
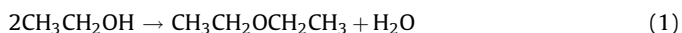
Thermally stable and insoluble silver salts of 12-molybdophosphoric acid with varying amount of Ag cations were prepared. XRD results indicated the presence of single phase of Ag<sub>x</sub>H<sub>3-x</sub>PMo<sub>12</sub>O<sub>40</sub> (0 < x < 3). FTIR and Raman results indicated that Ag was incorporated in the secondary structure of Keggin ion. The catalytic conversion of ethanol increased in the order of H<sub>3</sub>PMo > Ag<sub>2</sub>PMo > Ag<sub>1</sub>PMo > Ag<sub>3</sub>PMo. Pure H<sub>3</sub>PMo is highly selective to dimethyl ether formation; in contrast Ag<sub>x</sub>H<sub>3-x</sub>PMo<sub>12</sub>O<sub>40</sub> catalysts offered better ethylene selectivity. The pyridine adsorption studies revealed that increase of Ag incorporating led to increase the Lewis acid sites.

© 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

The utilization of ethanol from biomass fermentation instead of petroleum as chemical feedstock is considered as an alternative process that attracts the research worldwide. This alternative pathway could share in the reduction of CO<sub>2</sub> emission from the industries. Bio-ethanol is an attractive alternative feedstock to be used for the production of ethylene and diethyl ether. Ethylene is one of the major feedstock of the petrochemical industry. Production of petrochemicals from a non-petroleum, environmentally friendly feedstock and development of new, efficient ethylene production processes are considered as challenging research areas [1–3].

Aliphatic alcohols, with exception of methanol, have two modes of dehydration; bi-molecular dehydration to produce ethers and intra molecular dehydration to olefins as represented in Eqs. (1) and (2):



Both dehydration reactions of alcohols to give ethers and olefins are well known acid catalyzed reactions which proceed over

different solid acid catalysts such as H-mordenites, H-ZSM-5, H-beta zeolite and silica-alumina [4,5].

Heteropolyacid (HPA) catalysts were considered in the dehydration reaction of alcohols due to their higher activity than the conventional solid acid catalysts [6–8]. Recently, Ciftci et al. [9] applied tungstophosphoric acid impregnated MCM-41 catalysts for alcohol dehydration reaction. They observed 99.9% ethylene selectivity at 300 °C, with about 98% ethanol conversion. However, proton containing HPAs are highly soluble in polar and non-polar solvents, which retard their use as industrial heterogeneous catalysts.

It is well known that the protons in the secondary structure of HPA can be exchanged partially or completely with different metal cations (e.g., Cs<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and Ag<sup>+</sup>) without affecting the primary Keggin structure to prevent the HPA being leached. The catalytic behaviour of HPA metal salts attracts considerable interest, due to their multi-functional behaviour [10]. These salts are efficient in most of the reactions proceeded by acidic catalyzed processes [11]. The primary influence on the activity for alcohols to hydrocarbons is the concentration and strength of Brønsted acid centres presented in metal salts of HPAs [12].

Gurgul et al. [13] studied the effect of humidity on catalytic performance and stability of Ag<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. The authors observed that Ag<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> offered 99.8% ethylene selectivity and 70% ethanol conversion at 2% humidity and 220 °C reaction temperature. With the increase of humidity to 9%, the selectivity to ethylene was lowered to 99.2% at the same reaction temperature, but ethanol conversion was increased to 100%.

\* Corresponding author. Permanent address: Chemistry Department, Faculty of Science, Sohag University, Sohag 82524, Egypt. Tel.: +966 2 6400000/68987; fax: +966 2 6952292.

E-mail addresses: [ttali@kau.edu.sa](mailto:ttali@kau.edu.sa), [catalysa98@yahoo.com](mailto:catalysa98@yahoo.com) (Tarek T. Ali).

Thus, the authors concluded that the presence of water stabilized the surface composition of  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ . Matachowski et al. [14] reported the eco-friendly production of ethylene by dehydration of ethanol reaction using  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$  salt in nitrogen and air atmospheres.

Although,  $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$  has demonstrated high catalytic ability for the dehydration of ethanol to ethylene, its high acidity reduces its stability. In our previous study, we prepared copper salts of  $\text{H}_3\text{PMo}$  and the incorporation of copper resulted in an increase of the selectivity towards diethyl ether formation [15]. Motivated by the aforementioned findings, and our ongoing endeavours in the development of selective catalyst for ethylene production from ethanol, we report Ag-substituted  $\text{H}_3\text{PMo}$  solid acid catalysts for the selective dehydration of ethanol into ethylene. To best of our knowledge, the application of partially and fully Ag substituted  $\text{H}_3\text{PMo}$  catalysts for the aforementioned reaction has not previously been reported.

## 2. Material and methods

### 2.1. Materials

12-Molybdophosphoric acid ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$ ) (SD Fine Chemicals, India) and  $\text{AgNO}_3$  (Sigma–Aldrich, UK) were the starting materials to synthesize Ag-substituted  $\text{H}_3\text{PMo}$  salts. Ethanol 99.8% produced by BDH chemicals (USA) for preparative gas chromatograph (GC) was used as a reactant. Pyridine 99.9% produced by BDH chemicals (USA) for spectrophotometric measurements used as adsorptive material.

The catalysts of  $\text{Ag}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ , (where  $x = 1, 2$  and  $3$ ) were prepared by previously described procedures [16]. Stoichiometric amounts of aqueous silver nitrate salt were added slowly, by means of a burette, to an aqueous solution of 12-molybdophosphoric acid with constant stirring. The yellowish white precipitate was formed and it was aged in water bath for 72 h at  $40^\circ\text{C}$ . The dried powder was obtained after evaporation of solutions to dryness at  $100^\circ\text{C}$ . All the samples were calcined at  $300^\circ\text{C}$  for 3 h, in a static air atmosphere.

The sample code name was designed in the following code names: 12-molybdophosphoric acid =  $\text{H}_3\text{PMo}$ ,  $\text{Ag}_1\text{PMo} = \text{AgH}_2\text{P}-\text{Mo}_{12}\text{O}_{40}$ ,  $\text{Ag}_2\text{PMo} = \text{Ag}_2\text{HPMo}_{12}\text{O}_{40}$  and  $\text{Ag}_3\text{PMo} = \text{Ag}_3\text{PMo}_{12}\text{O}_{40}$ .

### 2.2. Techniques

Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were carried out on computerized Shimadzu Thermal Analyzer TA60 Apparatus (Japan). A Ceramic sample boat was used for TGA analysis. Sample weighing  $10 \pm 0.1$  mg was heated up to  $1000^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$  in a flow of  $40 \text{ ml min}^{-1}$   $\text{O}_2$  gas. For the DSC measurement, samples weighing  $5 \pm 0.1$  mg was heated up to  $500^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$  in a flow of  $40 \text{ ml min}^{-1}$ . X-ray powder diffractograms were recorded using a Bruker diffractometer (Bruker D8 advance target). Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.541838 \text{ \AA}$ ) was used as a constant source of radiation. The generator was operated at 35 kV and 20 mA, and diffractometer

at  $2^\circ$  diverting and receiving slits and a scan rate of  $20 \text{ mm min}^{-1}$ . FTIR spectra were obtained by the KBr disc technique in the wavelength range  $4000\text{--}400 \text{ cm}^{-1}$ , using Perkin Elmer Spectrum 100 FT-IR spectrometer spectrophotometer, the number of scans is 40, and resolution  $4 \text{ cm}^{-1}$ . The Raman spectra of samples were measured with a Bruker Equinox 55 FT-IR spectrometer equipped with a FRA106/S FT-Raman module and a liquid  $\text{N}_2$  cooled Ge detector, using the  $1064 \text{ nm}$  line of an Nd:YAG laser with an output laser power of 200 mW. Thermo Scientific Evolution 300 UV-spectrophotometer model with 10 mm matched quartz cell was used for all the absorbance measurements. 0.03 g of each sample was taken and placed in the quartz cell with 3.0 ml of pyridine in cyclohexane with initial concentration  $\approx 1.2 \text{ mmol/l}$ , the cell was covered with fitted quartz cover. The absorbance was measured as a function of time intervals from 1 to 270 min and measured each 5 min. The amount of adsorbed pyridine ( $\text{mmol g}^{-1}$ ) was measured by means of Beer's law as the follow:  $A = C \times \epsilon \times l$  where,  $A$  = initial absorbance – measured absorbance. So, the amount of adsorbed pyridine ( $C$ ) =  $[A/\epsilon \times l] \times (3/0.03)$  ( $\text{mmol g}^{-1}$ ). The calcined samples were subjected to a Pyridine (Py) adsorption analysis in a Fourier transform infrared (FTIR) PerkinElmer Spectrum 100 spectrometer. The analysis was carried out over samples disc which was treated under vacuum at  $1.33 \times 10^{-3} \text{ Pa}$  at room temperature. Later, the samples were treated with pyridine vapor and finally heated at  $150^\circ\text{C}$  under high vacuum for 30 min. The amount of Brønsted and Lewis acid sites was calculated via integration of the area of the IR spectral absorption bands showing the maximum values of intensity at  $1445$  and  $1542 \text{ cm}^{-1}$ , respectively.

### 2.3. Catalytic activity measurements

The catalytic reaction was carried out in a fixed-bed, flow type reactor with a flow system under atmospheric pressure. A 0.30 g catalyst sample was packed into a quartz reactor. Ethanol was carried by purified  $\text{N}_2$  as a carrier gas (5 mol% in  $\text{N}_2$ ) by an evaporator–saturator, placed in a thermostat. The total flow rate of ethanol in the feed gas stream was 1.5 L/h. The catalyst was heated up to  $300^\circ\text{C}$  at the rate of  $100^\circ\text{C/h}$  and activated in  $\text{N}_2$  for 3 h. All the reactions were carried out according to the same procedure where the catalyst was heated at a rate of  $1^\circ\text{C min}^{-1}$  to the reaction temperature. The products were analyzed by means of Varian CP-3800 gas chromatograph, Agilent technologies (USA).

The percentage conversion of ethanol and the selectivity towards ethylene are defined as follows:

$$\text{percentage conversion of ethanol} = \frac{\text{amount of ethanol converted/h}}{\text{amount of ethanol fed/h}} \times 100$$

$$\text{percentage selectivity of ethylene} = \frac{\text{amount of ethylene formed/h}}{\text{amount of ethanol converted/h}} \times 100$$

**Table 1**  
TGA and DSC data for dried  $\text{H}_3\text{PMo}$ ,  $\text{Ag}_1\text{PMo}$ ,  $\text{Ag}_2\text{PMo}$  and  $\text{Ag}_3\text{PMo}$  samples.

Sample	TGA data					DSC data					
	$T_{\text{max}}$ of decomposition steps ( $^\circ\text{C}$ )				No. of water molecules evolved/step				Endo-1 ( $^\circ\text{C}$ )	Endo-2 ( $^\circ\text{C}$ )	Exo-3 ( $^\circ\text{C}$ )
$\text{H}_3\text{PMo}^a$	129.45	240.32	351.64	420.10	10	2	1.5	–	182.38	360.80	385.32
$\text{Ag}_1\text{PMo}$	132.70	273.25	389.12	443.34	4.5	2.5	1	1	243.60	301.20	460.20
$\text{Ag}_2\text{PMo}$	124.18	234.70	357.40	451.13	1.5	3	2	0.5	243.90	308.10	475.67
$\text{Ag}_3\text{PMo}$	164.51	268.30	–	–	2.5	0.5	–	–	135.81	238.40	500.85

<sup>a</sup> Ref. [15].

Download English Version:

<https://daneshyari.com/en/article/227822>

Download Persian Version:

<https://daneshyari.com/article/227822>

[Daneshyari.com](https://daneshyari.com)