

## Selectivity limitations in the dehydration of glycerol to acrolein catalysed by Keggin-type polyoxometalates

Stefania Guidetti, Nicola Ballarini, Francesca Barone, Fabrizio Cavani\* and Marco Piccinini  
Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna, Viale  
Risorgimento 4, 40136 Bologna (Italy)  
\*fabrizio.cavani@unibo.it

### Introduction

Nowadays considerable efforts are being addressed to the study of new catalytic routes for the transformation of glycerol into chemicals [1,2]. In fact, in recent years the production of glycerol has been increasing, because glycerol is the co-product in the transesterification of triglycerides with methanol for the synthesis of biodiesel. An efficient process of transformation of glycerol into valuable chemicals would economically support the biodiesel producers. Current commercial uses of glycerol are limited to niche sectors; therefore, new catalytic routes, possibly for the synthesis of large-volume intermediates or even bulk chemicals, is a necessary condition in order to develop new commercial applications. One possible route is the double dehydration of glycerol into acrolein [3]; this reaction is thermodynamically more favored at high temperature, and hence the reaction has to be carried out in the gas phase, with solid acid catalysts. In the present work we report about the use of 12-molybdophosphoric acid, Keggin-type polyoxometalate, and of the corresponding cesium salt as the catalysts for the transformation of glycerol into acrolein, with the aim of identifying factors that limit the selectivity to the desired compound.

### Materials and Methods

Keggin-type heteropolyacid of composition  $H_4PMo_{11}V_1O_{40}$  and the corresponding Cs salt were used as bulk, unsupported catalysts. The compound of composition  $Cs_4PMo_{11}VO_{40}$  was prepared by addition of  $CsNO_3$  to an aqueous solution of the corresponding acid. The structural integrity of the compounds was checked by means of FT-IR and Raman spectroscopy. Catalytic measurements were carried out by vaporization of an aqueous solution of glycerol in a  $O_2/He$  stream, at 290°C. The mixture containing vapors of glycerol and water was fed to a glass reactor, with overall residence time of 0.2 s. The feed composition was the following (molar ratios): glycerol/oxygen/water/helium: 0.02/0.04/0.40/0.54; the reactor was loaded with 0.1 g of catalyst. The contribution of homogeneous reactions was rendered low, but non-negligible, by minimization of the void reactor volume. Indeed, glycerol thermally dehydrates to acrolein at above 350–400°C, and also gives rise to the formation of heavy compounds, such as ethers. Therefore, a preliminary study was aimed at the identification of those reaction conditions at which the contribution of homogeneous reactions was minimal; the optimal temperature range was comprised between 290°C and 350°C.

### Results and Discussion

Figure 1 reports the catalytic performance in glycerol dehydration of the Keggin-type polyoxometalate  $H_4PMo_{11}VO_{40}$ , as a function of temperature. Almost total conversion of glycerol was reached already at 300°C; however, a decline of conversion was observed at 360°C. This effect was mainly due to the total consumption of the limiting reactant, oxygen; however, some deactivation due to the accumulation of heavy compounds also contributed to

the activity decline. This phenomenon was less relevant when the partial pressure of oxygen in feed was increased.

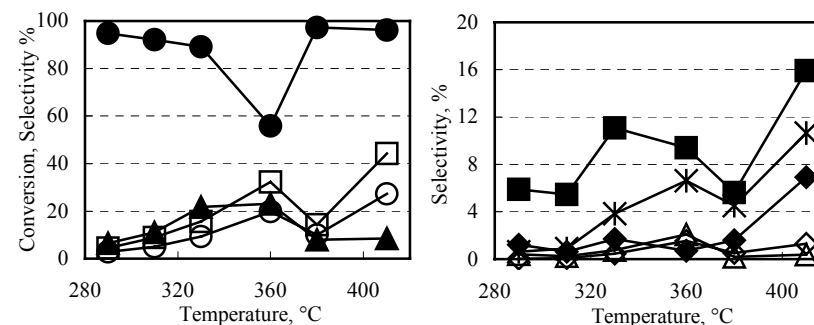


Figure 1. Effect of temperature on glycerol conversion and on selectivity to products. Catalyst: Keggin-type polyoxometalate  $H_4PMo_{11}VO_{40}$ . Symbols: glycerol conversion (●); selectivity to acrolein (■), acetaldehyde (\*),  $CO_2$  (○), CO (□), acetic acid (◆), hydroxyacetone (△), allyl alcohol (◇), and 1,2-propandiol + 1,3-propandiol (▲).

In the temperature range between 290 and 360°C, the main products identified were carbon oxides. The selectivity to acrolein was 11%. Moreover, there was a considerable amount of heavy compounds, as evident from the missing C in material balance. At above 360°C, the relevant contribution of homogeneous reactions overlapped to the heterogeneous one, making the conversion increase again. At high temperature a considerable amount of  $CO_x$  formed, but also the selectivity to acrolein was enhanced; moreover, the amount of heavies formed was lower than at low temperature. When the compound  $Cs_4PMo_{11}VO_{40}$  was used as the catalyst, at temperature lower than 360°C the selectivity to acrolein was less than that obtained with the corresponding Keggin acid, but also the amount of heavy compounds was lower. These data point out the importance of a control of catalyst acidity; in fact, acid sites were responsible not only for the formation of acrolein, but also of heavy compounds and of lighter  $C_2$  compounds. Moreover, homogeneous reactions contributed to glycerol conversion at temperature higher than 350°C.

### Significance

This communication reports about the main reactions involved in the acid-catalyzed dehydration of glycerol to acrolein, and the importance of a control of the catalyst acid characteristics.

### References

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