



## Comparison between catalytic and catalytic photo-assisted propene hydration by using supported heteropolyacid

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### ABSTRACT

Hybrid materials have been prepared by impregnation of the heteropolyacid H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> on commercial TiO<sub>2</sub>. The polyoxometalates (POM) amount deposited was 15, 30, 50 and 70% with respect to the weight of the TiO<sub>2</sub> support. Moreover two samples containing a POM amount of 15, and 50% with respect to the weight of SiO<sub>2</sub> were also prepared for the sake of comparison. All prepared samples were efficient catalysts for the hydration of propene to 2-propanol in gas–solid regime at atmospheric pressure and at temperatures ranging between 50 and 85 °C. The study carried out on the hybrid TiO<sub>2</sub> based materials evidenced that, as far as the catalytic activity is concerned, exists an optimum in the amount of POM. Notably the contemporary presence of heat and UV light improved the activity of the POM/TiO<sub>2</sub> and POM/SiO<sub>2</sub> materials, although POM/TiO<sub>2</sub> showed better catalytic and catalytic photo-assisted activity than POM/SiO<sub>2</sub>. POM species played a key role in both the catalytic and photo-assisted catalytic reactions, due to its surface acidity and ability to form strong oxidant species under UV irradiation. The presence of TiO<sub>2</sub> under UV irradiation improved the heteropolyacid performance supplying conduction band electrons to the POM.

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### 1. Introduction

The hydration of propene at ambient conditions is a reaction of great interest. The industrial propene catalytic hydration to 2-propanol is carried out at moderate temperatures (ca. 150–200 °C) and pressure (2 MPa) in the presence of an acid catalyst as phosphoric acid supported on silica, strong acidic resins [1], beta zeolite [2] and other acidic zeolites [3], whereas the reverse reaction, i.e. the dehydration of 2-propanol is a reaction frequently used for the characterization of the acidic character of catalysts, as for instance supported heteropolyacids. The last reaction gives rise to formation of propene at atmospheric pressure and temperatures ranging between 140 and 325 °C [4]. The propene hydration is not an easy reaction to be carried out, because thermodynamically limited by the mentioned reverse reaction at high temperature. Heteropolyacids, also called polyoxometalates (POMs), are catalysts industrially used for the hydration of propene to 2-propanol. POMs

are generally used in solution as acid and oxidation catalysts. They are very strong Brønsted acids and efficient oxidants that perform fast and reversible redox multielectronic transformations under mild conditions; consequently they can act as bifunctional catalysts [5]. The industrial hydration of propene to obtain 2-propanol has been carried out by using aqueous solutions of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. The catalytic reaction performed in gas–solid regime has been the object of several patents [6,7], but only very few papers have been published. Ivanov et al. compared the catalytic activity of acidic zeolite HZSM-5 with non-supported and supported H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (10% and 70% weight of POM on SiO<sub>2</sub>) for propene hydration reaction to obtain 2-propanol [8]. Supported POM resulted much more active than the bare corresponding sample and the HZSM-5, substantially due to their stronger acidity. The POM based materials showed a significant activity only from 100 °C. The maximum activity in hydration was measured at 130 °C, further increase of the temperature led to a decrease in the rate of 2-propanol formation due to the significant occurrence of the reverse dehydration reaction. The 70% POM/SiO<sub>2</sub> material showed a significant higher activity than the 10% POM/SiO<sub>2</sub> or the bulk POM.

Dispersing POMs onto solid supports with high surface area is generally useful to increase their specific surface area and hence catalytic activity. Acidic or neutral substances as SiO<sub>2</sub>, active carbon, acidic ion-exchange resin have been used as supports, whereas basic solids as Al<sub>2</sub>O<sub>3</sub> or MgO have been reported to induce POM

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