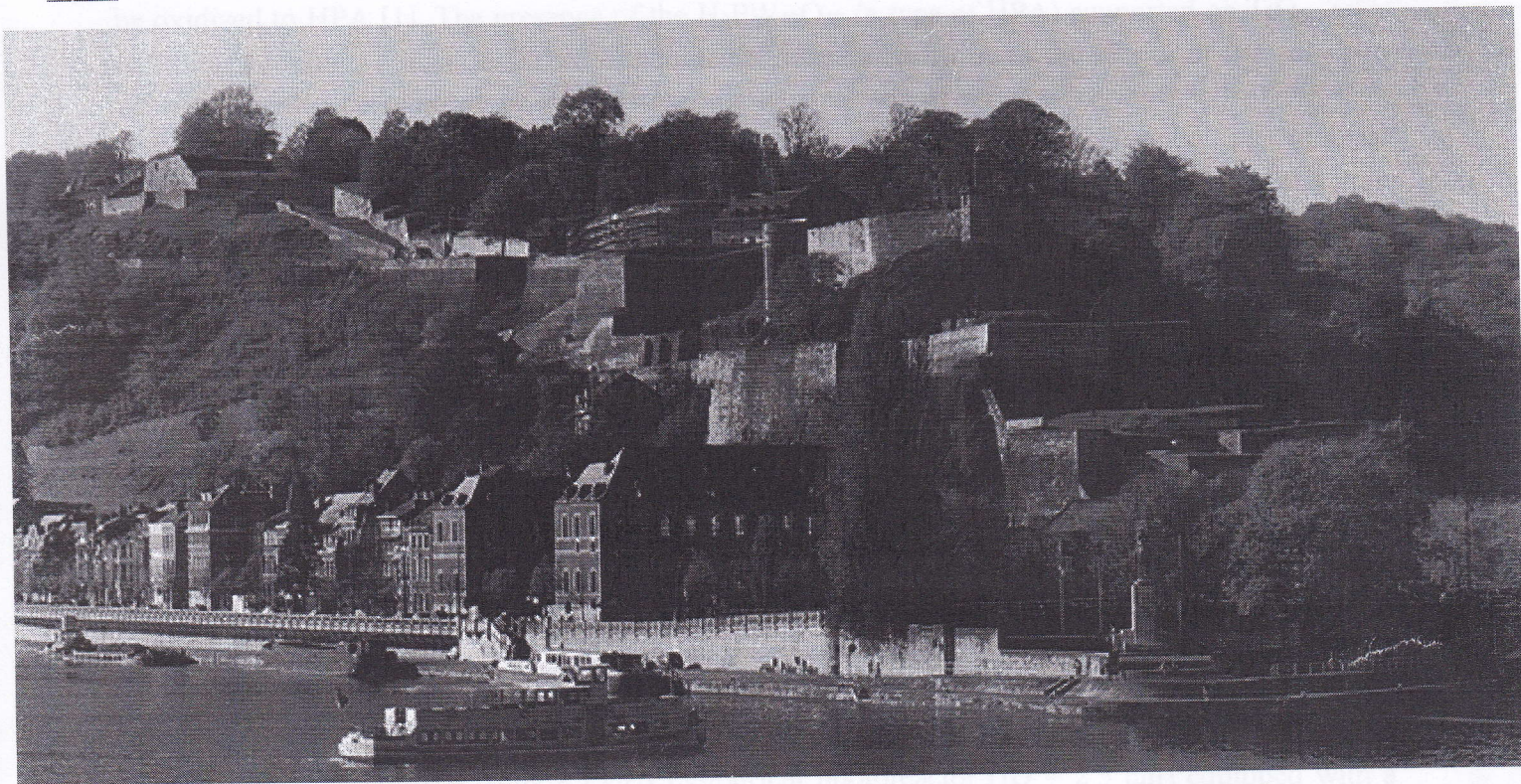


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# Keggin heteropolyacid supported on TiO<sub>2</sub> used in gas-solid (photo)catalytic propene hydration and in liquid-solid photocatalytic glycerol dehydration

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Keggin heteropolyacids (HPAs) are a wide class of discrete nanosized transition metal-oxygen clusters which are strongly acidic, oxidant and remarkably stable. They absorb light producing a charge transfer-excited state HPA\*, easily reduced to the relatively stable HPA<sup>-</sup> which in turn can be oxidized to HPA [1]. The presence of the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (a type of HPA) supported on TiO<sub>2</sub>, ZrO<sub>2</sub> or WO<sub>3</sub> has shown a beneficial role in photocatalytic reactions due to the ability of the activated HPA\* species to be reduced by the photoproducted electrons of the conduction band of the UV-activated semiconductor [2]. In this work two reactions have been performed: i.e. propene hydration and glycerol dehydration in gas-solid and in liquid solid regimes, respectively, and both of them were carried out in the presence of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> or H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> supported by impregnation on TiO<sub>2</sub>. Moreover, a binary material consisting of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> and TiO<sub>2</sub> was prepared also hydrothermally. Bulk and surface physico-chemical properties of the materials have been studied and the effect of light has been investigated by taking into account that the (photo) reactivity depends not only on the type of HPA but also on the preparation method, which influences the HPA features.

Propene hydration was carried out in a continuous photoreactor feeded with a flow rate of 20 cm<sup>3</sup>·min<sup>-1</sup> of propene and water (40 mM and ca. 2 mM, respectively). The runs were carried out at atmospheric pressure and 85°C. The reactor was illuminated with a 365 nm UVA- LED (irradiance in the 315-400 nm range: 50 mW·cm<sup>-2</sup>). 2-propanol along with diisopropylether was obtained in both catalytic and photocatalytic reactions and the presence of UV light improved the activity of all of the solids.

The photocatalytic dehydration of glycerol to form acrolein was carried out in liquid phase. The experiments were realized using a Pyrex cylindrical photoreactor (ID = 2.5 cm) equipped with a helium distributor device (Q<sub>He</sub>=200 cm<sup>3</sup>/min (STP)) and a magnetic stirrer to maintain 0.1 g of photocatalyst suspended in 40 g of pure glycerol. The photoreactor was externally irradiated by four Philips Black Light UV tubes (32 W, emission 365 nm). The gas phase was analyzed by GC-MS. The separation of acrolein from the liquid phase was achieved by heating the photoreactor up to 150 °C. In the presence of photocatalyst, the selectivity to acrolein ranged between 18 and 71%, and these figures resulted higher than that obtained in homogeneous medium (ca. 11%). The highest acrolein production has been obtained by using the H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> based materials.

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