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Author: Mohammad Jaber Darabi Mahboub Jordan Wright  
Daria C. Boffito Jean-Luc Dubois Gregory S. Patience



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# Cs, V, Cu Keggin-type catalysts partially oxidize 2-methyl-1,3-propanediol to methacrylic acid

Mohammad Jaber Darabi Mahboub<sup>a</sup>, Jordan Wright<sup>b</sup>, Daria C. Boffito<sup>a</sup>,  
Jean-Luc Dubois<sup>c</sup>, Gregory S. Patience<sup>a,\*</sup>

<sup>a</sup>*Department of Chemical Engineering, Polytechnique Montréal, C.P. 6079, Succ. CV  
Montréal, H3C 3A7 Québec, Canada*

<sup>b</sup>*University of British Columbia, 2329 West Mall, Vancouver, BC, Canada*

<sup>c</sup>*ARKEMA, 420 Rue d'Estienne d'Orves, 92705 Colombes, France*

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## Abstract

Heteropoly acids are among the best catalysts to produce carboxylic acids from light hydrocarbons. The Keggin structure maintains metals at a high oxidation particularly in the presence of cesium, vanadium, and copper. They effectively catalyze the partial oxidation of 2-methyl-1,3-propanediol (2MPDO)—a co-product in the hydroformylation of allyl alcohol to 1-4 butanediol. Converting 2MPDO to methacrylic acid would improve the economics of this route to 1-4 butanediol. Here, we establish the relationship between heteropoly acid performance and calcination temperature at 300 °C and 350 °C. The molybdenum oxidation state was higher after the high temperature treatment but it reduced to a greater extent during reaction (from Mo<sup>6+</sup> to Mo<sup>5+</sup>). The higher extent of reduction confirms the higher O<sup>2-</sup> → Mo<sup>6+</sup> charge-transfer in the Keggin anion. Maximum MAA and MAC selectivities were 61 % and 28 %, respectively at 250 °C after 480 min over cycling oxidation-reduction and 2MPDO/O<sub>2</sub>/Ar= 13/10/77 as the best reaction condition and feed composition. Though, the route of direct dehydration of 2MPDO (C-OH bond cleavage) followed by oxidation to MAC is the most direct path to the products detected, we propose a mechanism that passes through the homolytic dissociation of the tertiary C-H bond, in reason of the very similar bonding energies.

*Keywords:* 2-methyl-1,3-propanediol, Methacrylic acid, Mechanism,

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\*Corresponding author

*Email address:* gregory-s.patience@polymtl.ca (Gregory S. Patience)

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