

Selective Oxidation of Methacrolein over Strong Acid-Added Chromium Oxide Catalysts

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Methacrylic acid (MAA) has been practically produced by gas-phase oxidation of methacrolein (MAL) using phosphomolybdic acid as a catalyst. However, its catalytic performance, *e.g.* selectivity to MAA, is not satisfactory, and so the development of a novel catalyst is strongly desired. In this study, inspired by the stoichiometric liquid-phase oxidation with chromium species (Jones oxidation), we investigated selective oxidation of MAL to MAA over supported transition metal oxides combined with strong acids.

30 wt.% CrO_x/SiO₂ and MnO_x/SiO₂ were prepared by impregnation of Cr(NO₃)₃ and Mn(NO₃)₂ on SiO₂, respectively, followed by supporting H₃PW₁₂O₄₀ (HPW) on them. These samples are designated as HPW/MO_x/SiO₂ (M = Cr or Mn). Oxidation of MAL was performed in a fixed-bed flow reactor at 573 K. Molar gas composition was as follows; MAL: O₂: H₂O: N₂ = 3: 6: 13: 78. Reaction products were analyzed by using on-line gas chromatographs.

Fig. 1 shows conversion of MAL and selectivity to MAA for different catalysts. When MO_x/SiO₂ catalysts without HPA were used, MAA was not produced at all, but combustion reaction solely occurred. Nor HPW/SiO₂ produced MAA. In contrast to them, combined with HPW, MO_x/SiO₂ promoted the reaction for MAA formation. It should be noted that HPW/CrO_x/SiO₂ exhibited 63% selectivity to MAA at 16% conversion, while HPW/MnO_x/SiO₂ showed much lower selectivity to MAA.

Upon increasing HPW loading on CrO_x/SiO₂ up to 30 wt.%, both conversion of MAL and selectivity to MAA were improved. Further loading of HPW decreased the conversion of MAL with keeping selectivity to MAA constant. This is probably because too much loading of HPW terribly covered CrO_x particles, hindering the contact with MAL.

In the fresh catalyst, Cr³⁺ species such as Cr₂O₃ was dominantly present but after the reaction, Cr⁶⁺ was also found by XPS. During the reaction, in a similar behavior to Jones oxidation, a part of the surface Cr³⁺ species was oxidized to Cr⁶⁺, which then oxidized MAL together with HPW nearby (Scheme 1).

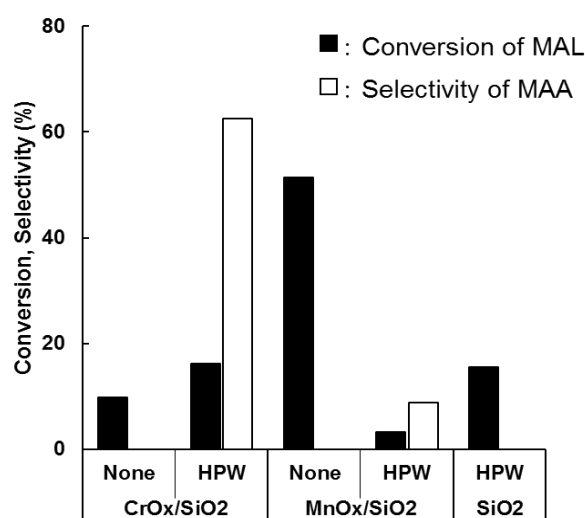
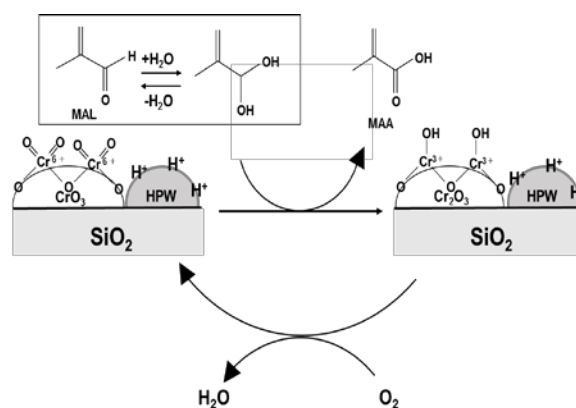


Fig.1 Reaction of MAL to MAA over different metal oxide catalysts.



Scheme.1 Plausible reaction mechanism.