

## Ethylene Carbonylation Revisited: New Paradigms

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While the hydroformylation of ethylene has been extensively studied, the (hydroxy/alkoxy) carbonylation of ethylene is far less prevalent in the literature. In particular, the literature scarcely discusses vapor phase or solid-supported catalysts for such reactions. Yet this approach offers a potentially industrially significant route for upgrading feedstocks. Our work focuses on studying ethylene carbonylation to yield propionate intermediates. Further processing these intermediates in turn offers a promising route to products such as the monomer methyl methacrylate. In collaboration with Northwestern University, The Dow Chemical Company has focused on identifying supported catalysts for ethylene (hydroxy/alkoxy) carbonylation, developing a mechanistic understanding of ethylene carbonylation, and optimizing reaction conditions. Specifically, we demonstrate a simplified mechanism explaining the role of iodide promoters and a Mo hydride intermediate underlying the operation of a highly productive supported  $\text{Mo}(\text{CO})_6$  catalyst with over 95% selectivity. When supported on HY zeolite by incipient wetness impregnation from pentane or by vapor deposition, turnover numbers for this catalyst increase dramatically. This is particularly dramatic for supports with low Si/Al ratios. These lower ratios promote more and stronger interactions between  $\text{Mo}(\text{CO})_6$  and the support, as evidenced by diffuse reflectance UV-visible spectra and thermogravimetric analysis. Via studies of this catalyst and others, we are improving our understanding of ethylene carbonylation and developing critical insights toward the development of the next generation of catalysts.