

Shell Hydroformylation (SHF)

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Hydroformylation or the “Oxo” reaction was identified by Otto Roelen in 1938 as an explanation for oxygenated byproducts during heterogeneously-catalyzed Fischer-Tropsch synthesis.^{1,2} The observed addition of carbon monoxide and hydrogen to olefins to form aldehyde and alcohol products was found to occur in the liquid phase, catalyzed by soluble cobalt carbonyl complexes leached from the heterogeneous cobalt catalyst under reaction conditions. The discovery ushered in a new era of “organometallic homogeneous catalysis”. In the early 1960’s, Slaugh and Mullineaux³ of Shell Oil discovered that addition of phosphines (σ -donors) provided for improved catalyst stability at low pressures. Ligand modification also provided the abilities to hydrogenate aldehyde intermediates to alcohols in a single step, and to control reaction selectivity via steric impacts.⁴ The phosphine-modified cobalt-catalyzed process became known as “Shell Hydroformylation” or SHF. The concept of ligand-modification was subsequently extended to catalysis by rhodium carbonyls for low-pressure hydroformylation.⁵⁻⁷

The ground-breaking Shell Higher Olefins Process (SHOP) made its debut in the late 1970s in the US. It opened up a new route to olefinic raw materials which serve as feedstock for SHF processes, to support the growing detergent industry. Detergent alcohol SHF products are used by customers to manufacture personal care products, soaps, shampoos and household cleaning solutions. Current Shell production is estimated at 1.2 billion pounds per year.

In 1999, SHF technology was leveraged to the hydroformylation of ethylene oxide⁸ to produce 1,3-propanediol (PDO), a monomer for production of a novel polyester polytrimethylene terephthalate (PTT). PDO nameplate production capacity is 160 million pounds a year. The new PTT polymer is finding commercial application in carpets and apparel.

References

1. J. Falbe, *Carbon Monoxide in Organic Synthesis*, Springer-Verlag, NY (1970).
2. R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).
3. L. H. Slaugh and R. D. Mullineaux, *J. Organometallic Chemistry*, **13**, 469 (1968); U.S. Patents 3,239,569 and 3,239,570 (1966).
4. C. A. Tolman, “Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis”, *Chem. Rev.* **77**, 313 (1977).
5. L. H. Slaugh and R. D. Mullineaux, US Patent 3,239,566 (1966).
6. D. Evans, J. A. Osborne, and G. Wilkinson, “Hydroformylation of alkenes by use of rhodium complex catalysts”, *J. Chem. Soc. A.* **33** (21): 3133–3142 (1968).
7. R. L. Pruett and J. A. Smith, *J. Org. Chem.*, **34**, 327 (1969).
8. J. B. Powell, L. H. Slaugh, T. C. Forschner, T. B. Thomason, T. C. Semple, P. R. Weider, J. P. Arhancet, US Patents 5,463,144; 5,463,145; 5,463,146 (1995).