

WATER-GAS SHIFT REACTION AND RHODIUM CATALYZED CARBONYLATION

For homogeneous systems the value of the water-gas change reaction is double. Firstly, it plays a key role in the Monsanto cycle in stabilizing the rhodium catalyst. Second, studies carried out in homogeneous systems employing metals other than rhodium have provided useful mechanistic insights into the heterogeneous water-gas shift reaction. We first discuss the catalytic cycle with 4.1 as one of the catalytic intermediates, and then mechanistic results that are available from an iron-based catalytic system. The catalytic cycle proposed for the water-gas change reaction during the Monsanto process is shown in Fig. Click here. The cycle occurs at acid pH, which is responsible for the generation of CO_2 which H_2 . In the absence of CH_3I , it has a useful function to stabilize the rhodium complex. The acetic acid – forming catalytic cycle ceases to exist in a situation where no CH_3I is available. Since the water-gas change process remains active however, rhodium remains in solution and does not precipitate out.

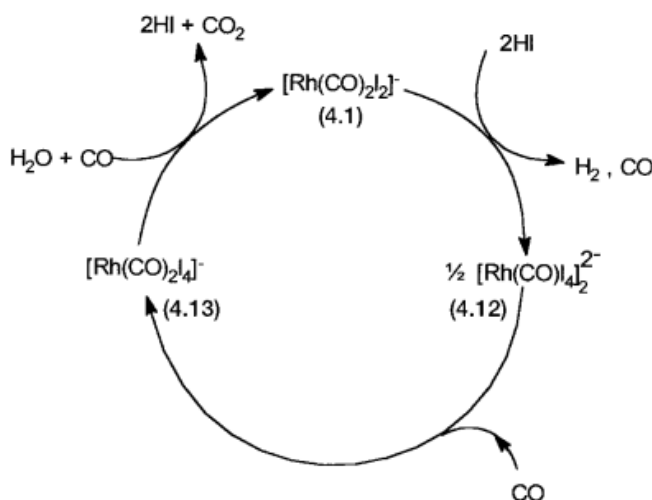


Figure. Proposed catalytic cycle for the water-gas shift reaction

At a molecular level there is no information known about the intimate mechanism for the water-gas change reaction with 4.1 as the precatalyst. The evolution of hydrogen in the conversion from 4.1 to 4.12 is possibly representative of the intermediacy of a hydrido complex. Similarly, in the conversion of 4.13 to 4.1, where HI and CO_2 are eliminated, nucleophilic attack on coordinated CO may be involved. Although these mechanistic conjectures are plausible, there is no direct evidence to support them. The water-gas change reaction with metal carbonyls as catalysts has also been studied under high pH. The catalytic cycle is shown in Fig. with $\text{Fe}(\text{CO})_5$ as the precatalyst. 4.6. This reaction with low turnover is carried out at $130\text{--}180\text{ }^\circ\text{C}$, under $10\text{--}40$ bar of CO , with alkali metal hydroxide as a promoter.

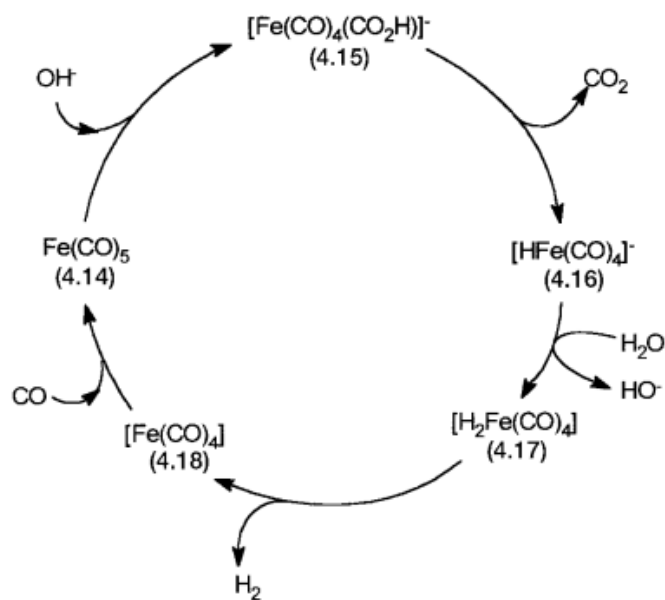


Figure 4.6 Proposed catalytic cycle for the water-gas shift reaction by $\text{Fe}(\text{CO})_5$

FISCHER–TROPSCH REACTION AND COBALTCATALYZED CARBONYLATION

The Fischer – Tropsch reaction, named after the original inventors, is basically the conversion of synthesis gas (CO H_2) to hydrocarbon mixture, and to a lesser degree oxygenated hydrocarbon. The commercial Fischer – Tropsch reaction like the one performed at SASOL in South Africa uses heterogeneous iron catalysts supported by potassium and copper. A wide range of hydrocarbons, containing one to more than 100 carbon atoms, are produced. Paraffins and to a lesser extent alkenes are the main products. These are thought to arise through carbide intermediates that are converted to CH_2 groups. There is no homogeneous Fischer–Tropsch catalyst that gives paraffin or alkene in good yield. The CO used for the carbonylation reaction contains also some hydrogen.

Due to the Fischer– Tropsch reaction catalyzed by the cobalt catalyst the side products in the BASF carbonylation cycle emerge. The high temperatures and pressures used in the BASF process are conditions under which the Fischer– Tropsch reaction with soluble cobalt catalyst can take place. In the Monsanto process the reaction conditions are much milder, and the side-product-forming Fischer–Tropsch reaction is avoided.

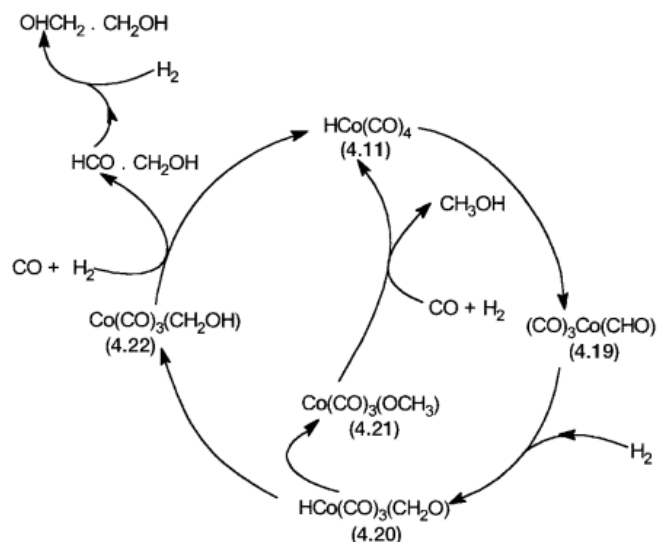


Figure. Proposed catalytic cycle for the Fischer–Tropsch reaction

The catalytic cycle shown in Fig is based on the known reactions of the cobalt carbonyls. Suggested to 4.7. The hydrido carbonyl 4.11 is converted to 4.19, a formyl species. Formyl complexes are considered to play a key role in all homogeneous catalytic reactions that give mainly oxygenated hydrocarbons from synthesis gas. Intramolecular CO insertion into a metal–hydride bond is thermodynamically unfavorable under mild conditions.