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Opinion

Water-Gas Shift Reaction: Advances and Industrial Applications

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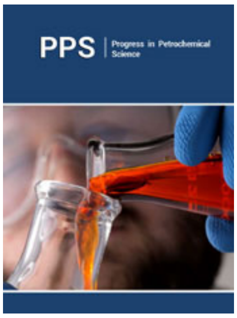

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Opinion

In industry, the water-gas shift reaction (WGSR) describes the reaction of CO and water vapor to form CO_2 and H_2, the two principal shift products:

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad \Delta H^o{}_r = -40.6kJ/mol \qquad (1)$$

As a stand-alone reaction, it is an important industrial reaction used in the manufacture of ammonia, to balance the H_2/CO ratio, and provide pure H_2 at the expense of CO. It is also an important side reaction that occurs in parallel to the main synthesis reactions in conjunction with steam reforming of methane (over Ni-based catalysts), and methanol synthesis from CO/CO_2/ H_2 mixtures (over Cu/ZnO/Al_2O_3) [1-4]. The WGSR is also a critical component in reducing CO concentrations from feed gas streams in proton exchange membrane fuel cells (PEMFC). The Pt electrodes are highly susceptible to CO poisoning to levels as low as 1ppm [5,6].

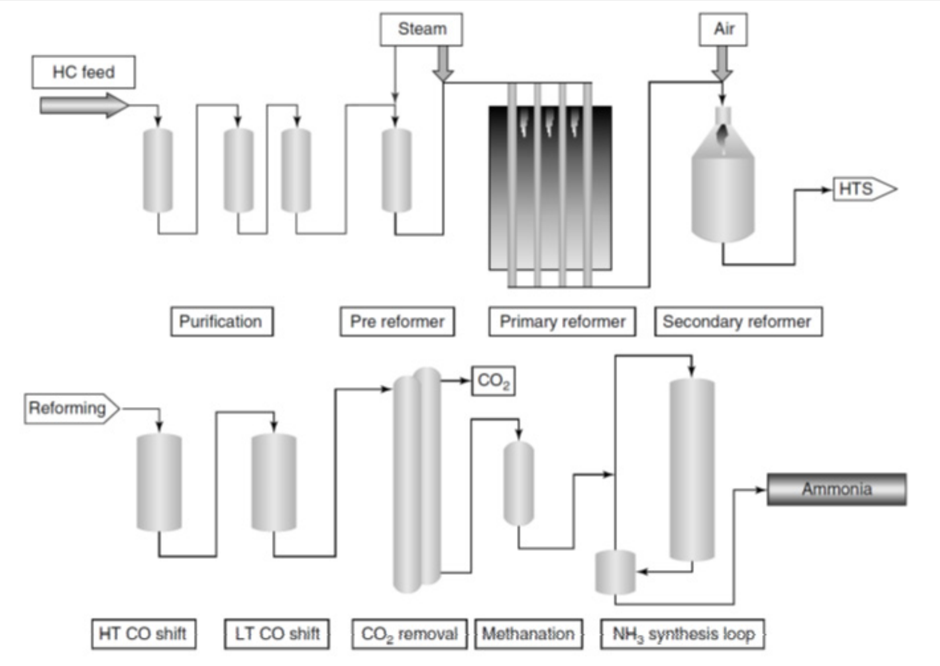

Figure 1: Syngas generation for ammonia synthesis: Steam reforming of natural gas, HTS converter unit, LTS converter unit [10].

In most ammonia plants, the shift conversion is carried out in two stages: A high temperature shift (HTS) conversion unit, which converts typically > 80% incoming CO, and a low temperature shift (LTS) conversion unit, which converts majority of remaining CO.

The HTS converter is typically operated at 310-450 °C, over a Cu-promoted Cr-Fe mixed metal oxide catalyst (with a composition of 88% Fe_2O_3/9% Cr_2O_3/3% CuO). At these temperatures, the shift reaction is in chemical equilibrium, and the concentration of CO at the reactor outlet is close to equilibrium levels, at 2-3% (v/v) at 400 °C. The LTS shift converter unit, over a commercial Cu/ZnO/Al_2O_3 catalyst (methanol synthesis catalyst), then converts majority of remaining CO, to a concentration of ~1000ppm (or, 0.1%). The inlet temperature of the gas stream entering the LTS converter unit is typically in the range of 190-230 °C and is operated in the adiabatic mode [7-9]. Due to the adiabatic nature of operation and the exothermal reaction, the temperature at the converter outlet can reach 280°C, and CO content is typically reduced to <0.1%. The schematic diagram of steam reforming (of natural gas) in series with the HTS and LTS water-gas shift conversion units, for syngas generation and purification for ammonia plants, is illustrated in Figure 1 [10].

The Cu/ZnO/Al_2O_3 WGS shift catalyst is highly susceptible to S poisoning, even at trace (or, ppb levels). Ahead of the LTS converter unit, a ZnO guard bed removes S (as H_2S) from the LTS inlet stream, typically operating at 370°C. The concentration of S leaving the guard bed is typically 10-50ppb, tolerant for the Cu/ZnO/Al_2O_3 shift catalyst.

We now consider and discuss the application of water-gas shift reaction for production of pure H_2, for use in proton exchange membrane fuel cells (PEMFCs). As stated above, the concentration of CO leaving the LTS converter unit is typically ~1000ppm or so (or, 0.1%). However, for applications in PEMFCs (for portable power generation or transport applications), the Pt electro-catalysts are highly susceptible to poisoning by CO, to levels as low as 1ppm. CO poisons the anodic Pt electrode through selectively adsorbing to Pt sites (akin to atom-specific CO chemisorption on Pt); however, CO poisoning is also slow and reversible. As possible strategies for mitigation, the use of CO-tolerant Pt alloy particles (based on Ru-Pt core-shell nanoparticles), a higher operating cell temperature (150°C), and use of oxygen co-feed in the fuel gas to the cell inlet, have all been proposed to combat the CO poisoning problem. In fact, the electrochemical oxidation of CO, adsorbed on the Pt electrodes, the so-called "CO stripping" reaction, is one of the most widely studied electrochemical reactions [11]. In addition, perhaps a better strategy is to reduce the CO content of the inlet stream from about 1000ppm to <1ppm before it enters the fuel cell assembly. A possible research advance in this area is the use of Ru-Pt core-shell nanoparticles and catalysts based on Au (supported on Fe_2O_3, TiO_2, etc.) for low temperature CO oxidation reactions [12-15]. The Au/TiO_2 system is exceptionally effective for catalysis of low-temperature CO oxidation reactions, even at temperatures as low as 0 °C, mainly on account of a unique particle shape (hemispherical shape), and a narrow particle size distribution (for nanoscale systems prepared by the D.-P. method, with TiO_2 Degussa P-25 support), with particle sizes in the range of 2.5-4.1nm. The unique particle shape and size leads to a very high metal-support interfacial contact area, a structural motif that is rich in coordinatively unsaturated sites (cus sites with a low coordination number, N), such as those at steps, corners, edges, and other planar/border discontinuities. The effect of a low coordination number for Au is enormous: In contradistinction with adsorption/activation characteristics of planar, metallic Au for O_2/CO, the cus sites can result in a site-specific adsorption of over 13-orders of magnitude, at low temperatures (0°C or higher), with very high turnover rates and very low activation barriers (<20kJ/mol). Indeed, the grand universality of catalysis by nanoscale Au and application to catalysis of low-temperature CO oxidation reactions extends to other organic reactions of small molecules, including the water-gas shift reaction, synthesis of vinyl chloride monomer, synthesis of hydrogen peroxide from H_2 and O_2, and others. As originally proposed and validated by further studies, nanoscale Au dispersed on suitable supports is an "uncommonly good" catalyst.

The production of pure H_2 for use as in PEMFCs for streams containing very levels of CO require catalysts with exceptionally high activity at low temperatures. Under these conditions, the WGS equilibrium is favoured, and stoichiometric conversions and chemical selectivity to products can be attained. As discussed above, Au nanoparticles supported on a suitable oxidic support such as Fe_2O_3, CeO_2, and TiO_2, highly active for low-temperature CO oxidation reactions, are also exceptionally effective for low-temperature water gas shift reaction [16-21].

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