3. CONDITIONS THAT INFLUENCE KINETICS OF CARBON DEPOSITION

As shown in Sect. 2, essentially all representative gasifiers operate under conditions in which carbon formation is thermodynamically possible in the hot-gas cooler and cleanup sections. However, such calculations do not take account of the kinetics of the gas equilibration or carbon deposition processes, since all chemical reactions are assumed to proceed sufficiently rapidly so that thermodynamic equilibrium is achieved. Typically, methods exist to increase or decrease the rates of reaction either through gas-phase modifications or by altering the surfaces on which carbon deposition is to take place. Furthermore, under some operating conditions, carbon formation can be significantly reduced by quenching the gas to minimize its residence time at temperatures where deposition occurs.

There is much controversy concerning the identity of the active catalyst for the disproportionation of carbon monoxide in steel systems.[8] The loss of catalytic activity of iron in the formation of carbon has been observed to be accompanied by conversion of the iron to Fe_3C.[12] Hydrogen was effective in reactivating the catalyst, supposedly by converting the Fe_3C back to iron.[12] However, there are some compelling arguments that the formation of Fe_3C is necessary before carbon will deposit.[13]

The poisoning effect of H_2S on carbon deposition reactions has long been known.[14–16] This compound is routinely added to gas mixtures of high carbon activity to reduce degradation that involves carbon deposition as a precursor to carburization.[2,17-21] It is generally assumed that the sulfide acts to reduce the catalytic activity of surfaces with respect to carbon deposition.[20] The presence of water vapor has also been reported to inhibit deposition of carbon,[21] but not necessarily catalytically. Rather, water vapor can react with the deposit to form gaseous products or shift the equilibria of reactions 1, 2, and 3 so as to reduce CO decomposition.[21] However, as discussed in Sect. 2, relatively large concentrations of water vapor would be required to materially affect carbon deposition in the typical gasifier.

The formation of stable surface layers of certain types of oxides has been shown to be effective in decreasing carbon formation and/or reducing the susceptibility to metal dusting (perhaps by preventing deposition on reactive surfaces). These oxides include chromia, silica, and, possibly, alumina.[1,22,23] This effect will be discussed in more detail when alloying effects on metal dusting are reviewed in Sect. 4. Some surface oxides, such as Fe_2O_3 and Fe_3O_4, and carbides can actually increase carbon formation.[3,8,9,24] In addition to oxidation effects, alloying or material selection and surface condition can also affect deposition by controlling the types of carbides that form or the phase distribution of the alloy components.[24] Surface roughness increases carbon deposition rates.[3,25] As may be expected, the surface crystallography can have an important effect (see, for example, ref. 26).