343b Deactivation Characteristics of Cr-Free Fe-Based High Temperature Water-Gas Shift Catalysts

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Hydrogen production has been the focus of increased interest due to its potential to be the energy carrier of the future. Water-gas shift reaction is of central importance to produce high-purity hydrogen. Generally, the high-temperature water-gas shift reaction (HTS) is conducted on Fe-Cr catalysts. However, these catalytic systems possess many drawbacks such as low activity at low temperatures and harmful effects of Cr^{6+} on human health. Thus, development of chromium-free catalytic systems, which has high activity and is operable over a wide range of temperatures and pressures, is necessary.

Deactivation characteristics are among the most important features of catalysts. Before use, Fe_2O_3 must be reduced to Fe_3O_4, which is the active component of Fe-based catalysts. The deactivation of Fe-based HTS catalysts can be classified basically in two categories, sintering of magnetite and poisoning from impurities. During HTS, Fe_3O_4 particles suffer from sintering. This process leads to a decrease of the total surface area and to an increase of the average crystallite size. Halogens and arsenic compounds are strong catalyst poisons, but normally they are unlikely to be present in the feed. In coal-based plants or those following cyclic reformers, however, traces of unsaturated hydrocarbons, oxygen, and nitric oxide can cause catalyst fouling by leading the formation of gum-like deposits, which prevent the access of the syngas to the internal catalyst surface. On the other hand, in coal-based plants the total amount of sulfur compounds, generally H_2S and COS, can be significant. Sulfur poisoning becomes a major issue.

In this work, Cr-free Fe-based catalysts promoted by first row transition metals and lanthanides were developed with a modified sol-gel technique. Catalytic performance was investigated using a simulated coal-derived syngas stream as feed. The sol-gel Fe-based catalysts demonstrate a significantly higher activity, stability, and sulfur tolerance than the conventional Fe-Cr catalyst. Deactivation characteristics of the catalysts, magnetite sintering and sulfur poisoning are studied using variety of techniques including BET, TPR, TPO, XRD, XPS, DRIFTS and TEM, applied before, after or during reaction.