
Question 21: What is the impact on unit performance when different qualities of hydrogen are used for the reduction step in a fixed-bed reforming unit?

BURTON (Motiva Enterprises LLC)

Hydrogen needs to be dry and have less than 20 ppm of contaminants such as water, light hydrocarbons, CO, CO₂, H₂S, and NH₃. Each of these can have different effects on the catalyst's final activity. The purpose of the reduction step is to remove the oxygen from the catalytic metals while minimizing chloride stripping. Contaminants either compete with this step or, for example, light hydrocarbons might react with the metal oxide forming CO, which will poison the platinum and result in lower activity.

LAMBIE (KBC Advanced Technologies, Inc.)

Charles covered most of it. I will add that the water strips the chloride from the catalyst, and it could lead to increased downstream corrosion. CO is a poison for the unreduced catalyst and will lower the activity. CO₂ is a precursor to CO. To a certain extent, hydrocarbons react with the metal oxides to form CO, which poisons the catalyst. My only other comment is that it would be ideal for the hydrogen medium to be electrolytic hydrogen, if it is available. Alternatively, hydrogen plant hydrogen is acceptable as long as the CO or CO₂ is low. A minimum of 90% purity should be used in all cases.

DUNHAM (UOP LLC, A Honeywell Company)

All I want to add is that UOP recommends electrolytic hydrogen for promoted catalyst.

SCOTT LAMBIE (KBC Advanced Technologies, Inc.)

A good hydrogen reduction of the catalyst is one key to the proper operation of a reforming unit. A good reduction step dries out the catalyst, reduces the metals, and improves the metals dispersion while avoiding excessive stripping of chloride from the catalyst and low-pH corrosion of wet effluent equipment. The reduction step is done in a hydrogen atmosphere with adequate hydrogen partial pressure.

The hydrogen supply should be dry, contain no CO, CO₂, H₂S, or hydrocarbons heavier than ethane to prevent poisoning of the catalyst before the reduction is complete. Ideally, the H₂ purity should be greater than 90%. Electrolytic hydrogen and hydrogen from a hydrogen plant with a low CO content are

recommended sources of reduction hydrogen.

The main problems associated with different qualities of hydrogen used for the reduction step differ depending on the impurities present. Hydrocarbons, particularly propane and heavier hydrocarbons in the reduction gas, can react with residual oxygen and the metal oxides on the catalyst to form CO. CO is a catalyst poison for the unreduced catalyst, and the result is a lower activity of the regenerated catalyst. Note that any recycle gas driers should not be put online until after the initial reduction step as hydrocarbons or CO/CO_x may be present.

Water present in the reduction gas will increase stripping of chlorides from the catalyst and inhibit metals reduction. This will result in increased corrosion in the regeneration system and will slow up the line-out period after oil-in. Water is generated in the reduction process, so it is important to regularly drain all low point drains to remove water that is formed in the process. Alternately, recycle gas drying can be used once initial reduction is complete. This will also speed up the line-out period.

H₂S will also inhibit reduction, so presulfiding is done after the reduction is complete. Ideally, any high H₂S or SO_x should be detected and eliminated before the final reduction. This is done with a desulfation step to enable good oxychlorination. H₂S can still be produced during the final reduction step, so H₂S levels should be monitored. If high H₂S levels are seen, then a decision must be made as to whether a second desulfation step is justified, though this is rare. Typically, high H₂S at this stage is a result of iron scale buildup in the system and reactors and may indicate a need to clean the equipment and/or screen the catalyst.

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