Water effect on the new catalyst of high temperature shift conversion during first reduction

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Abstract

The water–gas shift reaction plays a major role in ammonia and hydrogen plant design and operation. Good performance of the shift catalysts, and attainment of a close approach to equilibrium and, hence, minimization of the CO slip from the catalyst system is critical to the efficient and economic operation of the plant and ensures maximum hydrogen production from the hydrocarbon feedstock. Excessive drying out of catalyst during first reduction was studied to identify its influence on the catalyst during normal operation.

Keywords Shift conversion catalyst · Catalyst reduction · Ammonia plant · Hydrogen plant · Water effect

Introduction

The water gas shift reaction is an essential step in modern ammonia plants. Efficient and reliable shift conversion is required to ensure that the highest yield of hydrogen can be obtained from the reformed hydrocarbons. Hence, good performance of the shift catalyst and attainment of equilibrium CO slip from the catalyst system is critical for the efficient and economic operation of the plant to maximize the hydrogen production from the plant. In most ammonia plants, the shift conversion is carried out in two stages. Usually, a high temperature shift (HTS) catalyst is used as the first stage and typically converts over 80% of the CO. A low temperature shift catalyst (LTS) then converts the majority of the remaining CO [1]. As well as maximizing the hydrogen production, the water gas shift reaction also maximizes the CO₂ production from an ammonia plant. In addition, carbon oxides, both carbon monoxide and carbon dioxide (CO_x), are a poison to the ammonia synthesis catalyst and, therefore, must be removed. CO is converted into CO₂ for easier removal in the CO₂ removal system. CO₂ is an essential component for the Urea plant [1].

The high temperature shift (HTS) catalyst is comprised of iron oxide, with a chromium oxide stabilizing agent to

reduce the rate of sintering of the active iron crystallites at high temperatures [2]. More recently, copper has been added to the formulation to increase the activity per unit bed volume and to provide protection against catalyst over-reduction at low steam–gas ratios [3]. Typical operating temperatures for a high temperature shift catalyst are between 310 and 460 °C and at this temperature, a new catalyst charge should be able to reduce the CO level at the reactor exit close to the equilibrium level of the process conditions, usually in the range 2–3 mol%. At these temperatures, iron has sufficient activity to deliver the required performance.

Virtually, all high temperature shift catalysts are in the form of pellets of Fe₂O₃/Cr₂O₃/CuO, with 88%, 9%, and 2.6%, respectively. A small level of residual impurities are from the manufacturing process, primarily sulfur (production specification < 0.025 wt%, typically < 0.01 wt% for 71–5) [4]. The active phase of iron oxide is magnetite, Fe₃O₄, and so the catalyst must be reduced to the fully activate the catalyst. The reduction of a high temperature shift charge normally occurs at the same time as the reduction of the reforming catalyst, as both process gas and steam are needed for a controlled reduction to occur. The equilibrium point is controlled by the H₂O/H₂ and the CO₂/CO ratios. It is important to have steam present as a part of the reduction process as it moderates the reduction effect. Otherwise, the catalyst would over-reduce to metallic iron. It can be shown that if the H₂O/H₂ ratio exceeds 0.18 at 400 °C, then the desired magnetite is the stable phase [1, 4].

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Ammonia plant in fertilizer Company has high temperature shift converter with catalyst volume about 60 m³ with two beds, the two-bed catalyst was changed during turn-around by another new catalyst batch of (Johnson Matthey catalyst). During first reduction of primary reformer and high temperature shift conversion, the catalyst bed temperature of high temperature shift converter increased sharply for few minutes. In this short note, we will discuss this phenomenon to identify its influence on the catalyst life time and performance during normal operation.

Case study

Normal high temperature shift conversion catalyst reduction [5, 6]

- Purge the reactor free of air with inert gas.
- If possible, heat the catalyst bed with dry gas until the process gas condensation temperature is exceeded. Alternatively, heat the catalyst with process gas and allow the effluent gas to go to the vent. Pressurization to system pressure can be carried out at any time during the reduction. The process gas and steam flow combined should give a space velocity of approximately 200–1000 h⁻¹.
- Raise the catalyst temperature to 300 °C at up to 50 °C per hour. Reduction begins around 150 °C.
- The CO shift reaction will begin around 300–320 °C and the observed temperature rise will depend upon the inlet CO content and steam–gas ratio. The inlet gas must contain less than 15% CO (wet basis) because the maximum allowable temperature at this stage is 500 °C. A typical composition of dry gas would be 68% H₂, 14.5% N₂, 14% CO, 1.5% CO₂, and 2% CH₄ [1].
- Raise the inlet temperature to at least 370 °C and hold for several hours. This allows any residual sulfur from the manufacturing process to be converted into H₂S and driven off. This temperature should be held until the sulfur level has removed or reduced to the enough level 0.5 ppm according to the next reaction in the desulfurization unit:

The hydrogen sulfide can be converted into zinc sulfide by passing through zinc oxide catalyst.

Sulfur is considered poison for the low temperature shift conversion catalyst. The desulfurization period should be only 4 h from the first introduction of gas.

- Adjust the bed inlet temperature and process gas rate to operating values. The catalyst is now fully activated and

the process gas can now be passed forward to the next step.

Excessive increasing of catalyst temperature during first reduction

Hydrogen plant in fertilizer CO. has high temperature shift converter with two beds each bed has a catalyst volume 30 m³ and has thermo elements on the inlet and outlet and catalyst beds as shown in the Fig. 1, the new catalyst batch charged in august 2014 while the plant was started up on 5 October (due to shortage in Natural gas in EGYPT).

High temperature shift catalyst reduction was started with heating up for front end by N₂ circulation was started on 5th October 2014 and continued to 7th October 2014 (for about 37 h), N₂ circulation was stopped on 7th October 2014 at 1:30 a.m., steaming for front end was started by adding two tons of steam to the N₂ circulation and the steam condensed in 306E003 this two tons of steam continued to about 10 min, then steam flow increased to 25 tons at the same time of N₂ Circulation stoppage steam flow was 25 ton/h. for about 20 min and then increased to 35 ton/h. After increasing the steam flow to 35 ton/h, 25 min later, it was observed that the catalyst beds temperature increased sharply as shown in the Table 1.

Fig. 1 High temperature shift conversion catalyst

Table 1 Temperature profiles of high temperature shift catalyst during reduction

Thermo element no.	Starting temperature	Highest temperature
TT-304002	266	308
TT-304003	260	330
TT-304004	277	452
TT-304005	233	347

As shown in the above table, the maximum temperature jumped was (TT-304004) outlet temperature of second bed.

When the plant operated at load about 90%, the performance of high temperature shift converter in terms of delta P and CO slip were in acceptable level, which means the catalyst was not affected by shooting up of catalyst bed temperature during steaming or first catalyst reduction. The temperature profile of catalyst was close to the design temperature.

Phenomena discussion

Under normal conditions, the surface of the fresh high temperature shift conversion catalyst is covered with hydroxyl groups. After the catalyst exposed several hours to N₂ circulation during first reduction at temperatures seen in during heating up the high temperature shift conversion catalyst, the hydroxyl groups are stripped away leaving very active Fe–O–Fe groups on the surface of the catalyst [6]. This surface readily rehydrates when steam is introduced prior to introduction of process gas, releasing heat [5]. Only a small portion of steam reacts with the surface and the most of the steam acted as a heat carrier. This means that the bottom layer of the catalyst was heated up not only by rehydration of the catalyst surface, but also by the heat carried down from the top layer of catalyst. This phenomenon only affects the fresh catalyst during first reduction. During first reduction of high temperature shift catalyst to magnetite form, which has different surface properties to the hematite in fresh catalyst [6, 7].

Recommendations

A care should be taken that if fresh catalyst is exposed to warm dry nitrogen for many hours, the surface of the catalyst will be dehydrated and subsequent rehydration can cause a spectacular exothermic. The exothermic start-up can be avoided by making sure the catalyst is not excessively dried.

If it is necessary for circulation with nitrogen for a long time, the following should be considered:

1. Add a small amount of steam to nitrogen to prevent the drying.
2. Temporarily discontinue the nitrogen circulation.
3. Lower the HTs inlet temperature.
4. If a catalyst has been dehydrated, the size of the subsequent exotherm can be minimized by a high flow to remove the heat generated. Alternatively, steam can be introduced intermittently in pulses with time allowed between pulses for the exotherm to subside.

Conclusion

Shift catalyst beds temperature increased sharply during steaming for front end after heating up for front by nitrogen for about 37 h. This exotherm is due to rehydration of the catalyst by steam. This exotherm do not normally cause any catalyst damage. However, some recommendations suggested avoiding excessive drying out of high temperature shift conversion catalyst.

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