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Summary of Methanol Synthesis Catalyst Replacement

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Abstract: catalyst replacement involves a series of work, such as passivation, unloading, loading, temperature rising and reduction. The operation of each stage determines whether the follow-up work can be carried out smoothly or not, and directly affects the operation status, consumption and capacity of the unit after start-up. Jinmei Jinshi Chemical Industry Investment Group Co., Ltd Taking the methanol synthesis catalyst replacement of kt / a methanol plant in June 2019 as an example, the operation process of catalyst passivation, catalyst unloading and loading, catalyst temperature rise reduction and other links involved in the replacement process is introduced in detail. The operation (operation) experience of each link involved in the methanol synthesis catalyst replacement is summarized, and the corresponding improvement suggestions are put forward according to the existing deficiencies In the future, the replacement of methanol synthesis catalyst can be completed with high quality and high efficiency.

1. Introduction

Jinmei Jinshi Chemical Investment Group Co., Ltd. Shijiazhuang cycle Chemical Industry Park Branch Company 200 kt / a methanol plant, a total of two methanol synthesis gas compressors, two compressors in parallel. The production capacity of phase I and phase II are 100 kt / a respectively, and the two phases share a set of methanol synthesis unit. The first phase of the plant was put into operation in March 2015 and the second phase was put into operation in November 2017. In June 2019, the annual overhaul opportunity of the whole plant will be used to replace the methanol synthesis catalyst. Catalyst replacement involves a series of work such as passivation, unloading, loading, temperature rising and reduction. The operation at each stage determines whether the follow-up work is carried out smoothly or not, and directly affects the reaction efficiency of methanol synthesis tower and the consumption and capacity of the system after the start-up of methanol plant. Therefore, it is necessary to summarize the experience and lessons of every catalyst replacement.

2. Structure of Methanol Synthesis Tower and Application of Catalyst

Methanol synthesis adopts 6.4 MPa low pressure synthesis process, and methanol synthesis tower adopts spiral tube straight pipe compound series external cooling structure produced by Chengdu General Engineering Technology Co., Ltd.; methanol synthesis tower is divided into upper and lower sections, the upper section is straight tube shell type, the lower section is spiral tube shell type, and the upper and lower sections are respectively set with steam drum to adjust the corresponding bed temperature[1].

The catalyst used in the synthesis tower of 200 kt / a methanol plant is megax NJ-1 catalyst produced by Nanjing Shide catalyst Co., Ltd. On December 20, 2013, all methanol synthesis catalysts were packed into the column, From August 12 to 16, 2014, the catalyst was heated and reduced, and since then, low-pressure nitrogen has been used for catalyst protection; on March 18, 2015, the methanol plant was officially put into production, and as of June 7, 2019, the methanol synthesis catalyst was operated for 4 years and 3 months; during the production process, the catalyst was carried out according to the situation of crude methanol synthesis reaction and the steam yield of steam drum The catalyst bed temperature was raised from 225 ℃ to 250 ℃.

3. Replacement of Methanol Synthesis Catalyst

3.1 Passivation of Catalyst

3.1.1 Catalyst Passivation Process

At 10:24 on June 7, 2019, the fresh gas was cut by methanol line, and the methanol synthesis system was combined with the first phase methanol synthesis gas compressor for circulating cooling and medium pressure nitrogen replacement. By 17:05 on June 7, the outlet temperature of methanol synthesis tower (trca40102 / trca40103) dropped to 97 ℃, and the outlet temperature of lower column (tra40108a / tra40108b) dropped to 101 ℃. Because the combustible gas content of methanol synthesis system cannot be replaced within a short time, the methanol synthesis system was disconnected from the methanol synthesis system, and nitrogen replacement was conducted between the methanol synthesis system and the methanol phase I compressor; at 23:39 on June 7, after the methanol synthesis system and the phase I methanol synthesis gas compressor were respectively qualified, the methanol synthesis system was connected with the phase I methanol synthesis gas compressor The system pressure is maintained at about 0.60 MPa, the carrier is nitrogen, and the inlet circulating gas volume is maintained at about 20000 Nm3/h.

At 02:00 on June 8, 2019, instrument air was slowly added from the inlet of methanol synthesis system. The oxygen content at the inlet of the system was controlled at about 0.2%, the outlet temperature of the upper and lower towers increased slightly, and steam was continuously emitted from the vent drum on site, indicating that oxygen had been added to the system and the catalyst began to be passivated; the oxygen content of methanol synthesis system was basically controlled at 0.2% from 02:00 to 09:00 on June 8, 2019 At 14:10 on June 9, the oxygen content at the inlet and outlet of methanol synthesis system reached about 20%, and the outlet temperature of the upper and lower towers did not rise any more. It was judged that the catalyst passivation was completed, and the passivation process took a total of 35 hours H (see Table 1 for details). During catalyst passivation, the pressure difference between the instrument air pipe network and the system inlet is small (the pressure of instrument air pipe network in the plant is 0.65 MPa, and the system inlet pressure is 0.58 MPa In order to ensure the smooth replenishment of instrument air, the system inlet pressure relief was conducted by opening part of the site (the main vent point is the pipeline from the water cooler to the separator for wax removal).

3.1.2 Summary of Catalyst Passivation Operation

(1) At first, due to the small pressure difference between the instrument air pipe network and the inlet of the system, the instrument air was introduced to the inlet of the first stage of the methanol compressor by using the pressure gauge of the instrument air storage tank at the inlet of the circulation section of the methanol phase I compressor for oxygen distribution. However, after the actual passivation, it was found that the supplement amount was too small to meet the required oxygen content In order to increase the pressure difference between the instrument air and the system inlet, the instrument air valve group is connected and the on-site venting is enlarged to reduce the system inlet pressure. It is suggested that before the next catalyst passivation, according to the status of the methanol synthesis compressor, the system inlet pressure can be reduced in advance by opening up the field venting, so as to facilitate the smooth replenishment of inlet instrument air.

(2) The analysis data of oxygen content at the inlet of the system has deviation, especially affected by the small amount of catalyst added in the early stage of passivation, which leads to some difference in the results of manual analysis. The field steam vent volume of the upper and lower tower drums and the data measured by the four in one portable detector are used for auxiliary judgment. It is suggested that the laboratory personnel summarize the analysis experience under the condition of low oxygen content to ensure the real-time and accurate data during passivation.

(3) From 11:00 to 14:00 on June 8, 2019, because the temperature at the outlet of the upper and lower towers did not change significantly, the field operator opened the inlet instrument air valve group, resulting in a sharp increase of air addition. In this stage, the temperature rose rapidly and the passivation reaction was severe, but the catalyst bed temperature did not exceed 200 ℃, which had no significant impact on the passivation effect. It is suggested that during the passivation period, especially in the initial stage of passivation, the amount of air added must be kept stable, and the duration should be longer, so as to avoid the dead angle in the system and ensure the stable temperature of the catalyst bed, so as to prevent the catalyst from sintering and agglomerating due to excessive oxidation reaction and increase the difficulty of subsequent unloading and treatment.

(4) The original planned time for passivation of catalyst was 44 h, and the actual time was 35 h. by checking the status of the catalyst discharged from the site, it was found that the catalyst did not agglomerate and catch fire in large area, indicating that the passivation was relatively thorough.

3.2 Unloading and Loading of Catalyst

(1) during the unloading process of the catalyst, the temporary pipe and discharge port are not smooth, and the flange joint has been adjusted many times, and there are some problems such as improper operation of the tools. It is suggested that we should be good at summing up experiences and lessons, and make preparations for corresponding tools and instruments in advance, so as to shorten the construction period.

(2) The catalyst in the lower column agglomerates, indicating that the rate control in the passivation process needs to be strengthened. It is suggested that the operation of catalyst passivation should be sorted out and the data should be sorted out to explore the appropriate rate control in the passivation process to avoid the occurrence of similar problems.

(3) During the catalyst unloading period, the upper column tubes were checked for smoothness by means of strong light flashlight and heavy hammer test. A total of 12 tubes (5 tubes in total) were found 455 tubes) were blocked. The bottom part was effective, but the middle part was ineffective. It was analyzed that the catalyst in the above-mentioned columns was powdered and compacted or bridged during the original loading. In order to avoid the recurrence of similar problems, the rubber hammer is used for vibration during the filling to prevent bridge erection[2].

(4) The φ 25 mm and φ 10 mm ceramic balls loaded this time are oval and non perforated (the

previous furnace is open-ended ceramic balls), and their strength is worse than that of the previous furnace. During the loading process, there are more cracks, which will easily cause the pressure difference of the synthesis tower to increase and block the filter in the future operation. It is suggested that the ceramic balls with higher strength should be considered in the selection of ceramic balls.

(5) Since there is no boiler water during the catalyst unloading, the leakage test of the upper column and the lower tower coil was not carried out. Only after the start-up is normal, the sampling and analysis frequency of drum continuous drainage can be increased to judge the leakage of methanol synthesis tower internals. It is suggested that relevant arrangements and preparations should be made during catalyst replacement, so as to carry out leakage test of upper tower tubes and lower tower coils, so as to avoid hidden dangers for future production.

3.3 Temperature Rise Reduction of Catalyst

The methanol synthesis catalyst in this furnace is C307 type methanol synthesis catalyst produced by Sinopec Nanjing Chemical Research Institute Co., Ltd. the catalyst is supplied in oxidation state (copper exists in the form of copper oxide). Therefore, it is necessary to reduce copper oxide to copper by heating reduction to obtain the active components required for catalytic reaction.

3.3.1 Preparation and Process of Temperature Rise Reduction

2.3.1.1 System Purging

The system purging before the catalyst temperature rise reduction can effectively avoid dust accumulation, reduce the pressure difference of methanol synthesis tower during the production, and prevent the catalyst dust from being carried to the crude methanol filter and distillation system.

In the process of catalyst loading, before sealing the manhole of the lower tower, lay a tarpaulin with a diameter of 3.6 m above the coil of the lower tower, and hold the pressure by using the phase II methanol synthesis gas compressor (this time, start the phase II methanol synthesis gas compressor, and conduct the commissioning work of the methanol synthesis gas compressor), until the pressure is 1.0 At MPa, open the inlet quick cut valve (uv40101) to blow off the catalyst powder and ceramic ball powder on the upper tower; after the purging, close uv40101, and the compressor of methanol synthesis gas compressor will hold pressure again, and the pressure will rise to 1.0 After MPa, repeat the above steps until the catalyst powder and ceramic ball powder of the upper tower are obviously reduced, and then close the manhole of the lower tower; after that, purge the lower tower with the same method and steps; after the purging, install the outlet pipe again. In the process of purging, the lifting belt should be tied at the bottom outlet of methanol synthesis tower to avoid large area dust dispersion.

2.3.1.2 Preparation Before Temperature Rise Reduction

(1) The leakage test of water cooler (c002a / b) was completed. Before the start-up, one water cooler tube in the South and 12 tubes in the north were plugged.

(2) The nitrogen replacement of the system is qualified, and the air tightness test is qualified (the leakage test is conducted by boosting the system with medium pressure nitrogen to 2.0 MPa).

(3) The instrument and safety interlock system in the system are qualified and function is normal.

(4) Check whether the fire-fighting and gas control equipment and other safety facilities are complete and can be used normally.

(5) Utilities (circulating water, deaeration water, nitrogen, medium pressure steam, instrument air

and electricity) have been supplied normally.

(6) The second phase methanol synthesis gas compressor operates normally.

(7) Inform the laboratory to prepare for analysis of temperature rise reduction of methanol synthesis catalyst.

2.3.1.3 Temperature Rise Reduction Process

After nitrogen replacement of methanol synthesis system is qualified, the water cooler (c002a / b) was put into operation on site. It was found that the return water butterfly valve could not be opened when it was put into use. After field disassembly and inspection, it was found that the gear of the actuator was damaged. All the actuators were removed and the valve plate was opened with pipe tongs. At 06:30 on July 19, 2019, the methanol synthesis tower was connected with the phase II methanol synthesis gas compressor. The start-up ejectors of the upper and lower towers were opened to heat up the catalyst. The heating rate was controlled at 10-15 ℃ / h. until 16:00 on July 19, the catalyst bed temperature of the upper and lower towers were increased to 170 ℃ and then kept constant temperature[3]. At 22:30 on July 19, after the hydrogen in the pipe network was qualified, the system adjusted the hydrogen. After the hydrogen distribution, the CO2 accumulation was analyzed at the outlet (carbonate was added during the production of the catalyst, and the carbonate reacted with hydrogen after hydrogen distribution to release CO2 to bubble and increase the specific surface area of the catalyst). Then, the system was opened to vent and discharged, and the medium pressure nitrogen at the inlet was used for pressure supplement to ensure that the system was in The outlet pressure was maintained at 0.7-0.8 MPa, and the inlet gas volume was about 23 000 m3 / h.

The temperature rise and reduction rate of the catalyst is determined by the water yield and hydrogen content at the outlet of the circulating gas: when the catalyst bed temperature is constant, if the hydrogen content at the outlet of the circulating gas increases continuously while the water yield decreases, it indicates that hydrogen does not participate in the reaction at this temperature, and the bed temperature needs to be increased slowly; if the hydrogen content at the outlet of the circulating gas is not accumulated and the water outlet is stable, the inlet hydrogen supplement shall be maintained If the hydrogen content at the outlet of the circulating gas does not accumulate and the water yield decreases significantly, it indicates that the hydrogen content is low, and the inlet hydrogen content should be increased. In the process of temperature rising and reduction of catalyst, the temperature of hydrogen replenishing valve and catalyst bed should be adjusted according to the above principles, and the process should be slow and stable.

At 02:00 on July 22, 2019, the hydrogen concentration at the inlet and outlet of the methanol synthesis tower is equivalent, and there is no water generation. The total physical and chemical water yield is 8.477 2 T. the actual water yield is close to the theoretical water yield (the theoretical water yield is 56.9 × 15% = 8.535 when the theoretical water yield is 15% of the catalyst loading amount) t) It shows that the temperature rise reduction of catalyst is completed and the whole heating reduction process takes 66 H (see Table 3 for details). Subsequently, the upper and lower towers were cooled to 210 ℃ for nitrogen replacement; at 06:30 on July 22, fresh gas was connected to the inlet of methanol synthesis gas compressor, and the methanol synthesis system entered into low load production state[4].

3.3.2 Summary of Temperature Rise Reduction of Catalyst

(1) the preparation of the catalyst before heating and reduction is not enough. The failure of the water cooler return valve is found later. If it is debugged ahead of schedule, it will expose the problem early, and lay a good foundation for heating reduction operation. It is suggested that the

equipment or valve of utility system should be debugged in advance in order to find problems and deal with defects in advance.

(2) The initial hydrogen distribution temperature of the catalyst is 170 ℃ and the temperature is too high. According to the previous operation experience and the phenomenon in the actual process (during the hydrogen extraction process at 06:30 on July 20, 2019, the temperature of the catalyst bed rose to 240 ℃, the hydrogen was cut off, and the drum was opened for venting on site), which should be at 130 ℃ The opening and effectiveness of the hydrogen make-up valve were explored to prevent the catalyst bed from “flying temperature” caused by the excessive opening of the hydrogen replenishing valve.

(3) The theoretical effluent rate of catalyst temperature reduction should be controlled at 100-150 kg / h. in the actual effluent process, the effluent rate is larger in the early stage and smaller in the later stage. The deviation between the peak value and the trough value of the effluent rate is large. The reason is that the analysis of sample is not timely and the adjustment is not timely, which leads to the instability of effluent rate control. It is suggested to summarize, improve and refine the operation, so as to accumulate experience for the future temperature rise reduction operation of catalyst.

(4) The operator training is not in place, and the control principle of temperature rise reduction is not firmly grasped, resulting in the corresponding relationship between hydrogen gas volume and catalyst bed temperature rise and effluent rate is not well controlled and the adjustment is not timely. It is suggested that the training of operators should be strengthened so that the operators can master the control principles and methods of temperature rise reduction.

4. Conclusion

The replacement of methanol synthesis catalyst involves many operation links, and the operation of each stage determines whether the follow-up work can be carried out smoothly or not, and directly affects the operation status and consumption of the unit after start-up. For the replacement of methanol synthesis catalyst, first of all, solid theory and principle should be taken as the basis of operation control. Secondly, the operation adjustment should be guided by theory, control principle and experience in the actual work, and the experience summary and transmission should be carried out for each link of the replacement work, so as to facilitate the high-quality and efficient completion of methanol synthesis catalyst replacement in the future.

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