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Commercial application of titania-supported hydrodesulfurization catalysts in the production of hydrogen using full-range FCC off-gas

Shaohu Wang[a,b], Binglong Shen[b], Lianglong Qu[b,*]

[a]*SINOPEC Wuhan Branch, Qingshan, Wuhan 430082, China*
[b]*Beijing Haishunde Titanium Catalyst Co. Ltd., A-1 North East-Ring Road, Beijing Economic-Technological Development Area,*
Beijing 100176, China

Abstract

This paper provides an alternative for low-cost feed used for on-purpose hydrogen production. Full-range FCC off-gas was applied to steam-reforming process as feed after treating with hydrogenation and hydrodesulfurization catalysts. Commercial run results were reported with novel TiO_2-supported Mo-based catalysts, T205A-1 and T205. The processes of catalysts loading, sulfidation, start-up and long-term run were described in details. Long-term run showed that TiO_2-supported Mo catalysts have good low-temperature hydrogenation activity, excellent HDS activity, and outstanding stability. Use of FCC off-gas as feed for hydrogen production is quite promising and will increase margins for refiners today.

Keywords: Catalyst; Hydrodesulfurization; Hydrogenation; Off-gas

1. Introduction

To meet the more stringent transportation fuel regulations, refiners will need more hydrogen. The hydrogen required mostly comes from two sources, catalytic reformers and "on-purpose" hydrogen plant. More than 85% of hydrogen production from "on-purpose" units is still generated using hydrocarbon steam-reforming technology [1]. Lighter feeds, such as methane (natural gas) through naphtha and refinery off-gases can be converted into hydrogen by either steam-reforming technology or gasification technology (partial oxidation). The heavier fractions, such as vacuum residue, deasphalter bottoms, refinery sludges, and petroleum coke can only be processed into hydrogen using gasification technology [2,3].

Due to the limited supply of natural gas and naphtha, refinery off-gases are becoming an important alternative for low-cost hydrogen [3,4]. The hydrogen content ranges normally from 30 to 90% with a few of them as low as 10%. Typical compositions of refinery off-gases are shown in Table 1 [5]. Off-gases from hydrocracking (HC), hydrotreating (HT), and catalytic reforming (CR) units have been widely used in hydrogen production due to their simple treatment processes. Coker gas (CG) has also been applied to produce hydrogen using a process by former BDI (now part of SEI) [6].

Problems arise when using largely available FCC off-gas as low-cost feed for producing hydrogen. First, full-range FCC off-gas consists of 15–20 vol.% olefins. They must be treated to lower than 1 vol.% before entering the steam reformer. But hydrotreating will lead to severe overheating of the pretreating reactor, thus runaway of the system. Second, FCC off-gases contain relatively large amount of sulfur, part of which is in organic form. They must be totally removed to meet the demand of steam-reforming catalysts ($S < 0.5$ ppm). Last, the presence of around 0.5% oxygen can also affect the performance of hydrotreating catalysts. The only commercial application of FCC off-gases was reported

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* Corresponding author. Tel.: +86-10-6786-1166;
fax: +86-10-6786-9312.
E-mail address: qull@hsd-ti.com (L. Qu).

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Table 1
Composition of typical refinery off-gases[a]

	HC	HT	CR	CG	FCC
H_2	32	55.31	86.72	12.84	15.03
CH_4	20	16.57	4.47	58.94	22.10
C_2H_6	10	14.4	3.94	17.83	9.71
C_2H_4	0	0	0	4.88	10.65
C_3H_8	14	7.53	2.74	1.15	0.12
C_3H_6	0	0	0	1.24	0.61
C_4H_{10}	17	2.88	1.47	0.25	0.00
C_4H_8	0	0	0	0.27	0.00
C_5H_{12}	6	2.06	0.96	0.28	0.00
CO	0	0	0	0	1.52
CO_2	0	0	0	0.3	1.36
O_2	0	0	0	0	0.27
N_2	0	1.15	0	2.04	15.24
H_2S	5–30	5–30	5–30	5–30	5–30
S (organic)	0	0	0	100–200	100–300

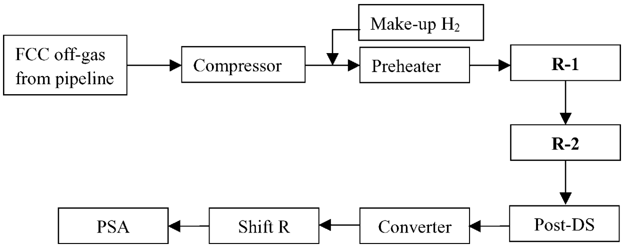
[a] Units are in vol.%, except O_2 in wt.%, S in ppm.

for hydrogen production in a refinery. However, the off-gas contained 6–15% of olefins, and the pretreating reactor must be quenched by cooled gas and recycling [7].

A novel process was developed by Haishunde and SEI to use full-range FCC off-gas as feedstock to produce hydrogen by steam reforming [8]. Parallel tubular reactors were used. Novel TiO_2-supported Mo-based catalysts, T205A-1 and T205 have been applied in the process. Through more than three-year commercial run, the catalysts showed high HDS activity, good low-temperature activity for olefin saturation and high stability. This paper described the commercial results of the catalysts used for the pretreatment of full-range FCC off-gas in the steam-reforming unit of SINOPEC Wuhan.

2. Reactors and catalysts

The system is designed for producing 5000 Nm^3 H_2 per hour by steam reforming. A schematic flow chart of the hydrogen production system is shown in Scheme 1. R-1 is an isothermal reactor with an inner diameter of 2.2 m, which contains 1205 parallel tubes with inner diameter of 39 mm and 6.5 m long each, used to saturate most of the olefins in the feed. The reaction heat is absorbed by steam in the shell before entering R-2. R-2 is an adiabatic reactor with an inner diameter of 1.2 m, used to further saturate the remaining olefins, and more important, to totally transfer the organic sulfur compounds into H_2S, which can be adsorbed by following post-desulfurization (Post-DS) agents. The main advantage of this configuration is that when FCC off-gas with high concentration of olefins passes through the two reactors, outlet olefin concentration can be controlled to lower than 1%; organic sulfur compounds can be totally converted to H_2S, which can be absorbed by ZnO to lower than 0.5 ppm. Thus, various feeds with different olefin contents can be used to meet the demand of steam reforming.



Scheme 1. Flow sheet of hydrogen production in Wuhan.

Table 2
Properties of catalysts

	T205A-1	T205
MoO_3 (%)	8.26	8.99
NiO (%)	2.40	
CoO (%)	1.02	1.64
Pove volume (ml/g)	0.21	0.22
Surface area (m^2/g)	111	104
Side crush strength (N/mm)	16.6	14.0
Attrition (%)	0.50	0.56

T205A-1, a Ni–Co–Mo catalyst, was loaded in R-1 and T205, a Co–Mo catalyst, was loaded in R-2. Before reaction, they were presulfided with CS_2 under certain conditions to ensure better performance of the catalysts, although the catalysts can be used without presulfidation. The properties of the catalysts were listed in Table 2. Micro-reactor results showed that TiO_2-supported T205 has much higher HDS activity than its Al_2O_3-supported counterpart (Table 3). Therefore, T205 can be operated at much lower temperature to achieve the same HDS level.

2.1. Catalysts loading

T205A-1 was loaded in reactor R-1. The total weight of T205A-1 loaded is 7700 kg. The loading density is 854.6 kg/m^3. T205 was loaded as three layers in R-2. Between each two layers, the catalyst was separated by ceramic balls with diameter of 6 mm. On the top and bottom of R-2, ceramic balls with different diameters were used to make better flow distribution and to support the catalyst. Totally, 5700 kg of T205 was loaded in R-2 with an average loading density of 912 kg/m^3.

Table 3
Comparison of HDS activity between TiO_2- and Al_2O_3-supported CoMo catalysts

Catalyst	Support	Thiophene conversion at different temperature (wt.%)		
		250 °C	300 °C	350 °C
T205	TiO_2	36.0	61.0	92.9
Reference[a]	Al_2O_3	16.9	23.0	39.5

[a] The reference catalyst contains the same level of Co and Mo as T205.

2.2. Catalysts presulfidation

The two catalysts in R-1 and R-2 were sulfided at the same time. Presulfidation was performed under a pressure of 0.5 MPa (at R-1 inlet). The system was first heated up to a certain temperature, then the sulfiding agent CS_2 was injected into the line. The cycle gas rate was 5000 m^3/h, and the purified hydrogen was between 33 and 55%. Total CS_2 injected to the system was 633 kg. By weighing the water formed during sulfidation and calculating the theoretical sulfur contents of the catalysts, 83% of sulfidation degree was reached during presulfidation.

2.3. Start-up

Following the above presulfidation, conversion process and start-up were carried out at the same time. As the conversion temperature rises, the increasing of the temperature in the two reactors and the hydrogen addition take place at the same time. When the heat from MTS outlet brings the catalyst bed up to about 180 °C, feedstock with high olefin content reacts as soon as it is injected into the reactor and the hydrogenation and conversion is in the proper conditions.

The unit was commissioned on 13 February 2000. At the beginning, due to the lack of outer source hydrogen, the hydrogenation feed used was non-penetrating gas, which contained only 13% of hydrogen and 20% of olefins. Therefore, it was insufficient in amount and the enrichment of hydrogen was needed. But after normal production, the hydrogen from the system can provided hydrogen source. Then full-range FCC off-gas can be injected to the system. The hydrogenation took place under the feeding temperature of 178 °C, which indicates the good low-temperature activity of T205A-1/T205. At 200 °C, the saturation of olefins is higher than 99.5%. This is much lower than conventional Al_2O_3-supported catalysts, which starts hydrogenation above 250 °C. For HDS of organic sulfur compounds, the temperature required for Al_2O_3-supported catalysts usually exceeds 280 °C. This is one of the advantages of our TiO_2-supported catalysts.

Under much milder conditions, all the organic sulfur compounds can be easily converted to H_2S. After treatment with ZnO, the outlet concentration of sulfur after Post-DS is always lower than 0.5 ppm, which meets the need for the conversion catalyst. Even though there is quite some amount of CO and CO_2, no methanation reaction was observed. Tables 4 and 5 listed the typical results from commercial run. In Table 5, gas composition before HDS reactors was collected and analyzed from FCC off-gas pipeline, while gas composition after HDS reactors was referred to that after the post-desulfurization treatment.

Table 4
Operating parameters of the HDS reactors

Flowrate of FCC gas (Nm^3/h)	3452
R-1	
Added H_2 (Nm^3/h)	357
Inlet temperature (°C)	277
Outlet temperature (°C)	243
Pressure drop (kPa)	1.9
R-2	
Inlet temperature (°C)	221
Outlet temperature (°C)	335
Pressure drop (kPa)	2.72

Table 5
Gas compositions before and after HDS reactors[a]

	Before	After
H_2	21.31	28.68
O_2	0.62	0.00
N_2	15.03	14.89
CH_4	29.48	28.96
C_2H_4	11.81	0.00
C_2H_6	13.41	25.22
C_3H_6	0.42	0.00
C_3H_8	0.04	0.62
C_4H_8	0.03	0.00
C_4H_{10}	0.00	0.04
C_5^+	0.22	0.32
CO	1.15	0.60
CO_2	0.58	0.33
$\sum C^=$	13.86	<1
$\sum S$	20	<0.5
Total	100.1	100.0

[a] Units are in vol.%, except O_2 in wt.%, S in ppm.

After the above treatments, the clean stream was fed to the converter, followed by shift reactors and PSA process, over 99.9% purity of hydrogen was produced.

2.4. Long-term run

Due to the floatation in operation and feeds of the FCC unit, the feed for hydrogen production changed frequently. The sulfur content varied from about 10 to 2000 ppm, sometimes even 5000 ppm, although the control level was designed to be lower than 150 ppm. The olefin content varied from 10 to 22%. Therefore, several accidents took place during the three-year operation. However, the catalysts can bear the floatation of feeds and even runaway. The FCC off-gas always contained up to 2% of oxygen, but the catalysts remained stable. Conventional Al_2O_3-supported catalysts must limit the O_2, CO, and CO_2 to lower than 5 ppm.

Till now, the unit has been on-stream for over three years and the reactor inlet temperatures were not raised yet. The TiO_2-supported catalysts rendered all the incidents and showed outstanding long-term stability in the full-range FCC off-gas pretreatment for the production of hydrogen. The catalysts showed very good low-temperature hydrogenation activity and excellent HDS activity. This takes the lead in the commercial application of pure TiO_2-supported catalysts in a refinery.

3. Economy evaluation

The original feed for hydrogen production in Wuhan was propane and feed consumed was 3.5 ton propane per ton of hydrogen. If the price of propane was counted to RMB 3000 Yuan, then the feed cost was RMB 10,500 Yuan per ton of hydrogen. After revamping, full-range FCC off-gas is used instead of propane. Although feed consumed is 4.5 ton FCC off-gas per ton of hydrogen, higher than using propane, considering the price of FCC off-gas as RMB 800 Yuan, the feed cost will only be RMB 3600 Yuan per ton of hydrogen. If the unit is to produce 7200 ton hydrogen per year, the refinery will save RMB 49.68 Million Yuan.

This process paves a new path for using the low-cost FCC off-gases to produce hydrogen to meet the increasingly needs of hydroprocessing in refineries today. Therefore, it won the second prize of SINOPEC Sci-Tech Award in 2002. Many refiners in China are going to apply it to their hydrogen plants.

4. Conclusions

By choosing the proper process and catalysts, full-range FCC off-gases can be used to produce hydrogen with steam-reforming technology at a low cost after pretreatment to lower the olefins and sulfur contents. This provides refiners with more hydrogen to their hydroprocessing units to meet the cleaner fuel specifications.

TiO_2-supported Mo-based catalysts have been successfully used in the pretreatment of full-range FCC off-gas for steam reforming. The catalysts showed much higher hydrogen and HDS activities at rather lower temperature, and good tolerance to impurities in refinery off-gases than their Al_2O_3-supported counterparts.

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