

PHF-101 Diesel Oil Hydrofining Catalyst

Science & Technology Management Department, CNPC

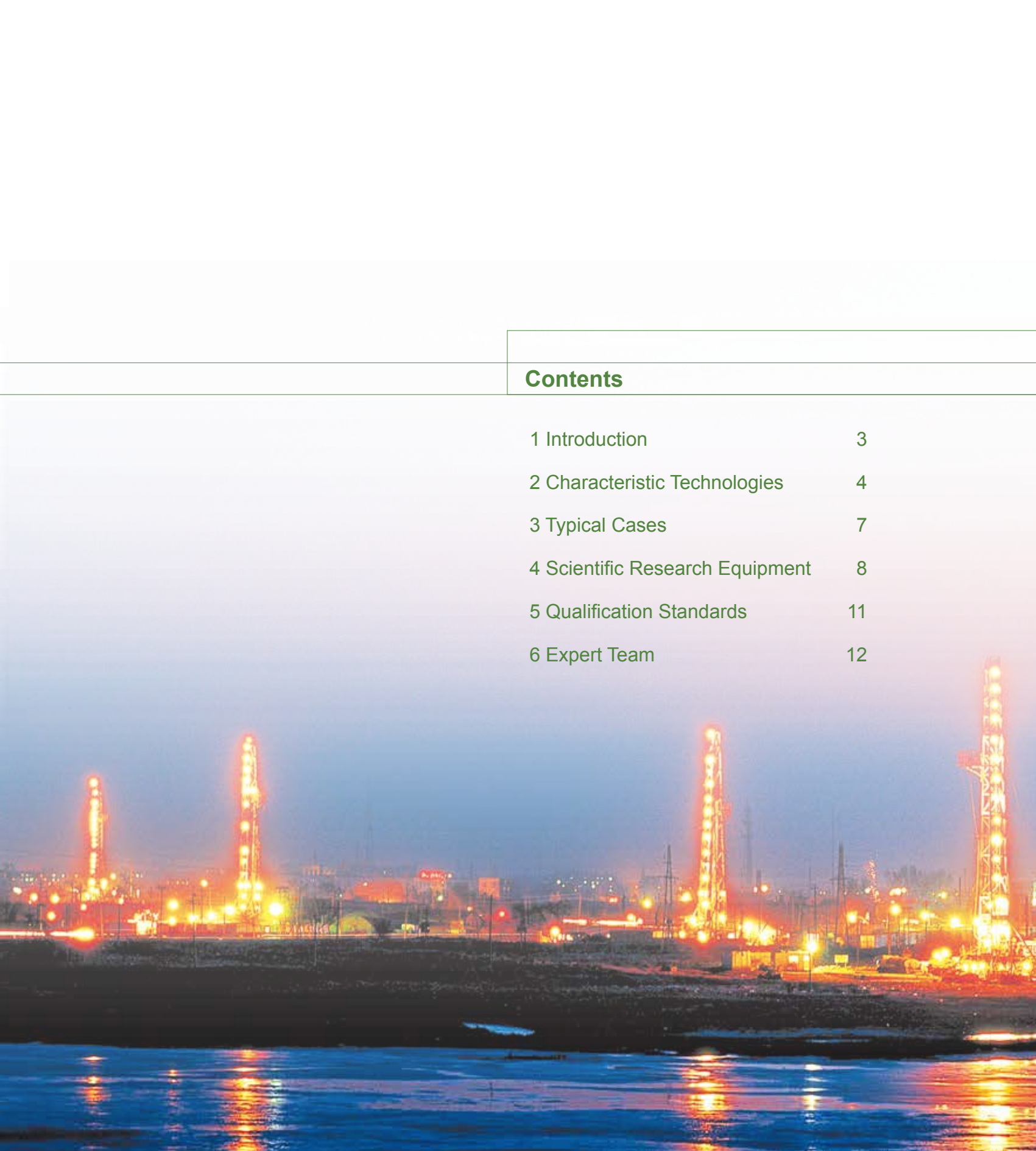
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CHINA NATIONAL PETROLEUM CORPORATION

*PHF-101 : New Environmental Protection
Diesel Oil Technology!*





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China National Petroleum Corporation (CNPC) is a state-authorized investment agency and a state holding company. On July 1998, with the implementation of the Institutional reform of the State Council, CNPC was reorganized to become an integrated oil company of cross-regions, cross-industries and cross-countries, it adopts modern enterprise system to realize the integrations of upstream and downstream operations, internal and external trade, production and marketing. CNPC's business covers six main sectors: oil and gas operations, petroleum engineering service, petroleum engineering construction, petroleum equipment manufacturing, financial services and new energy development. In 2014 CNPC produced 113.67 million tons of crude oil and 95.46 billion cubic meters of natural gas, while crude processing volume reached 150.2 million tons. The total revenue of RMB 2,730 billion with a profit of RMB173.4 billion had been achieved the same year.

CNPC was ranked 3th among the world's largest 50 oil companies and 4th in Fortune Global 500 in 2014.

CNPC strictly follows by the combined strategies of increasing resource capacity, expanding market shares and consolidating the international role, and persists in regarding technical innovation as a key framework to advance technological progress. To develop its core businesses, focuses will be placed on the solutions of key bottleneck technologies and key proprietary technologies. Thanks to continuously improving of the technical innovation system, optimizing the configuration of technological resources and strengthening the construction of strong talent teams, CNPC's technological creativity has been considerably upgraded. Consequently, a large number of technologies have been developed independently, with its own intellectual property.

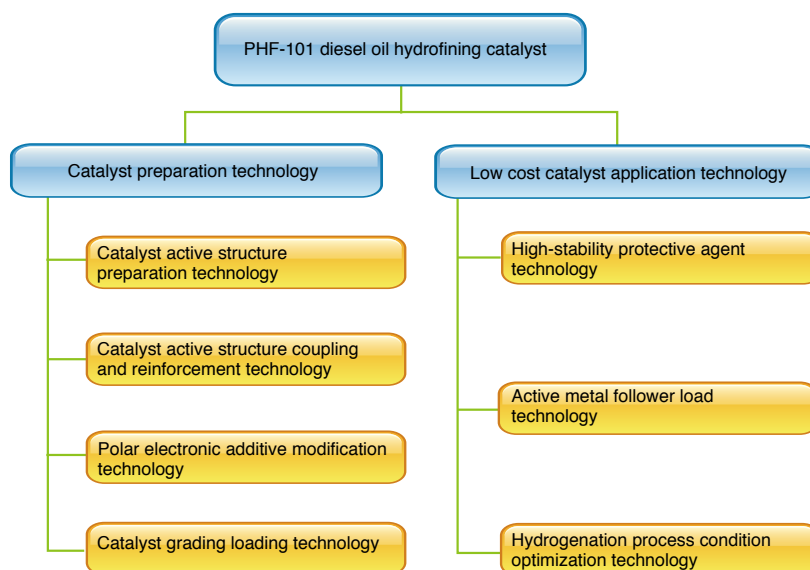
The PHF-101 diesel oil hydrofining catalyst is one of representatives for major innovations of CNPC.

OFFERING ENERGY SOURCES, CREATING HARMONY

1

INTRODUCTION

Hydrogenation technology is the most effective means of producing clean diesel oil. High performance and low cost catalyst is the key to realizing high efficiency hydrogenation process and maximum enterprise benefits. According to global refining business development demand, CNPC has successfully developed PHF-101 diesel oil hydrofining catalyst. The catalyst has outstanding hydrodesulfurization performance, good adaptability to feedstock, high liquid yield and stable activity and is applicable to hydrofining of straight run diesel oil, secondary processing diesel oil and the mixed oil of straight run diesel oil with secondary processing diesel oil. PHF-101 diesel oil hydrofining catalyst has been successively applied in Daqing Petrochemical $120 \times 10^4 \text{t/a}$ diesel oil hydrofining unit and Urumchi Petrochemical $200 \times 10^4 \text{t/a}$ diesel oil hydrofining unit. The commercial operation data show that PHF-101 catalyst completely meets the diesel oil production technology demand of GIV and GV units. PHF-101 diesel oil hydrofining catalyst has formed 8 China invention patents and 1 technology secret.



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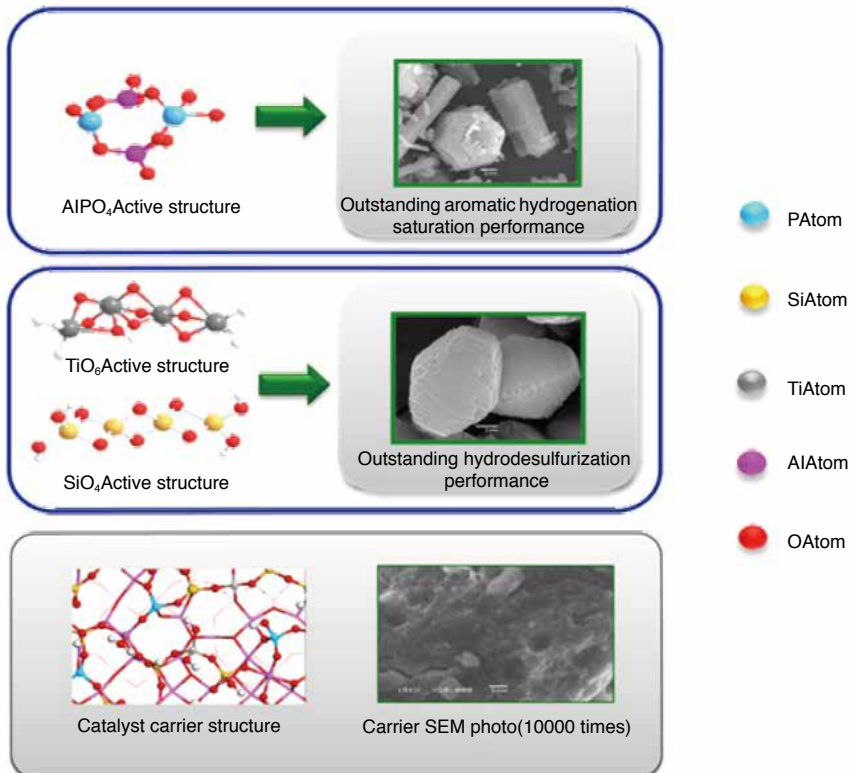
CHARACTERISTIC TECHNOLOGIES

2.1 Catalyst preparation technology

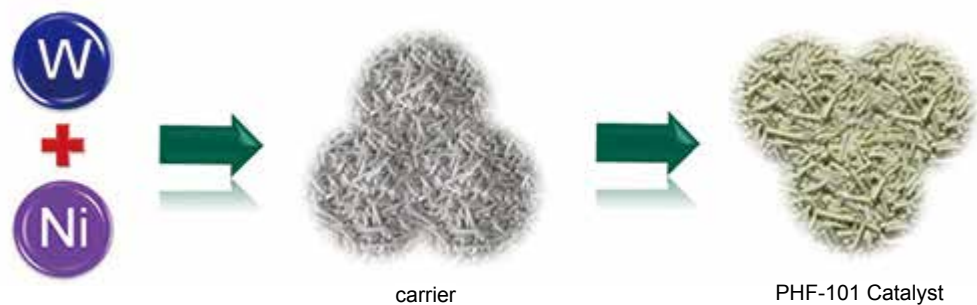
PHF-101 diesel oil hydrofining catalyst preparation: new catalyst materials of regular structure are used, and elements such as P, Ti and Si and AlPO_4 , TiO_6 and SiO_4 structure units are introduced in catalyst carriers, so that the catalyst forms more active centers favorable for steric hindrance type sulfide and aromatic hydrogenation to promote high efficiency removal of sulfur, nitrogen and aromatic hydrocarbon.



PHF-101 catalyst



- Polar electronic additive is introduced to adjust carrier acidity, eliminate strong acid center, weaken the impact of nitride on acid center, ensure diesel oil yield and reduce coking and carbon deposit while improving desulphurization efficiency.
- Structure modification additive is introduced in metal loading process to regulate active metal spacing and effectively promote orderly hydrodesulfurization, denitrogenation and aromatic saturation reaction



Typical physical and chemical property indexes	
Appearance	Clover
Diameter (mm)	1.3 ~ 1.7
Edgewise compressive strength (N/cm)	150 ~ 200
Pore volume (mL/g)	0.30 ~ 0.50
Specific surface area (m ² /g)	160 ~ 240
Stack density (kg/m ³)	0.70 ~ 0.90
Active components	Nickel, tungsten

2.2 Low cost catalyst application technology

The high stability protection agent technology for remarkably prohibiting catalyst bed pressure drop increase, the catalyst grading loading technology for maximally developing catalyst efficiency and the hydrogenation process condition optimization technology have been developed, thus greatly reducing the commencement cost and operation cost of catalyst and minimizing the enterprise’s production cost.



Operating conditions	
Reaction pressure (MPa)	≥
Volume space velocity (h ⁻¹)	1.0 ~ 2.5
Reaction temperature (°C)	≤ 5.0
Hydrogen to oil volume ratio (V/V)	300:1 ~ 500:1

3 TYPICAL CASES

3.1 Industrial application

PHF-101 diesel oil hydrofining catalyst found its first industrial application in Daqing Petrochemical 120×10⁴t/a diesel oil hydrofining unit in Sept. 2010. The processing feedstock of the unit is the mixed oil of coker gasoline, coker diesel oil and catalytic diesel oil. The unit is used to produce high-quality refined diesel distillate and ethylene cracking material naphtha distillate. The application result indicates that PHF-101 catalyst has excellent hydrogenation performance and good operation stability and completely meets the enterprise's production technology demand of GV diesel oil.

Item	Hydrofining diesel oil
Total sulfur (μg/g)	5.9
Cetane number	51.1
Desulphurization rate (%)	99.4
Diesel oil yield (%)	99.5
Up to GV diesel oil standard	

3.2 Diesel oil hydrogenation unit put into operation as per GV quality standard

PHF-101 diesel oil hydrofining catalyst was industrially applied in Urumchi Petrochemical new 200×10⁴t/a diesel oil hydrofining unit in Nov. 2011, and loading, drying and sulfuration of the catalyst all reached the requirements of the design. The unit was successfully started at a time. The product reaches GV diesel oil standard. The unit has become CNPC's first set of diesel oil hydrofining unit put into operation as per GV quality standard.



Refined diesel oil, raw oil, naphtha



4

SCIENTIFIC
RESEARCH
EQUIPMENT

Hydrogenation catalyst and process engineering test base

CNPC has an advanced hydrogenation catalyst and process engineering test base. The hydrogenation catalyst and process engineering test base has catalyst evaluation and process research platform, hydrogenation catalyst and catalytic material pilot scale-up platform, hydrogenation catalyst and catalytic material industrial scale-up platform and analysis and test platform.

4.1 Catalyst evaluation and process research platform

There are 67 sets of hydrogenation evaluation units at present:

- 20mL units (12 sets)
- 200 mL units (30 sets)
- 500 mL units (4 sets)
- 1L medium-scale units (three reactors, 2 sets)
- 1L medium-scale units (five reactors, 2 sets)
- 300mL units (gas phase, 2 sets)
- Liquid phase hydrogenation unit (1 set)
- Residuum hydrogenation units (15 sets)



Evaluation unit shop



1L four-reactor medium-scale hydrogenation
evaluation unit



Control room

4.2 Hydrogenation catalyst and catalytic material pilot scale-up platform

19 pieces/sets of molecular sieve synthesis, carrier and catalyst pilot units

- Molecular sieve pilot scale-up (1m^3 /batch);
- Catalyst pilot scale-up/ (40kg /batch).



Molecular sieve hydrothermal aging unit



1m^3 molecular sieve synthesis reactor

4.3 Hydrogenation catalyst and catalytic material industrial scale-up platform

Carry out an industrial scale-up test on the basis of pilot scale-up and then determine the production process flow and operation method of catalyst and catalytic material, thus establishing a foundation for industrialization and reducing process application risks.

- 6 finished catalyst production lines;
- Molecular sieve production capacity, 100t/a;
- Catalyst production capacity up to 5000t/a.



Rotary kiln



Banded extruder

4.4 Analysis and test platform

The platform undertakes the tasks including physical property test of catalyst and catalytic material, oil product analysis, catalyst/industrial unit calibration, etc. and is used to establish relevant analysis and detection methods.

- Totally 41 catalyst analysis and characterization instruments;
- Totally 66 oil product analysis instruments.



SEM



50L full automatic true boiling point distillation instrument

5 QUALIFICATION STANDARDS

Enterprise standard

PHF-101 ultra-low sulfur diesel oil hydrofining catalyst (Q/SY SHY 0015—2012).

Technology secret

A preparation method for high-activity diesel oil hydrogenation catalyst carrier material (20130264) .



Patents

- ZL 200410091492.6 A hydrogenation dearomatization catalyst containing aluminophosphate molecular sieves
- ZL 200410091490.7 A hydrodesulfurization catalyst containing molecular sieves
- ZL200610091158.X A diesel aromatic saturated hydrogenation catalyst and its application
- ZL200610091159.4 An aromatic saturated hydrogenation catalyst and its preparation method
- ZL200710064671.4 A γ - Al_2O_3 material with large specific surface area and its preparation method
- ZL200810114135.5 A preparation method for hydrofining catalyst with in-situ decomposition process
- ZL200810116715.8 A catalytic diesel oil hydrodearomatization method
- ZL001302841 A hydrofining catalyst and its preparation method



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EXPERT TEAM



Hu Changlu

Senior technical expert of CNPC, professor level senior engineer. He has been long engaged in the study and development of RHT technology. He has obtained 1 grade II national science and technology advance prize, 4 provincial and ministerial prizes and over 30 invention patents. 7 papers written by him have been published. He participated in preparing 1 monograph.

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Senior technical expert, professor level senior engineer. He has over 30 years of experience in R&D and production management of polyolefin. He has obtained 35 national, provincial and ministerial science and technology advance prizes. Over 50 papers written by him have been published. He has obtained over 30 patents.

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Senior technical expert, professor level senior engineer. He has been long engaged in R&D of refining and chemical catalysts and processes. He has obtained 4 CNPC science and technology advance prizes and 3 PetroChina technical innovation prizes. Over 60 papers written by him have been published. He has obtained 29 patents.

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Zhang Wencheng Senior technical expert. He has been long engaged in R&D of refining and chemical catalysts and processes. He has obtained 2 CNPC science and technology advance prizes, 2 PetroChina technical innovation prizes, 1 science and technology advance prize of Federation of Chemical Industry and 3 science and technology advance prizes of Heilongjiang Province. Over 50 papers written by him have been published. He has obtained over 20 patents.

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