PCA-1200

彼奥德电子
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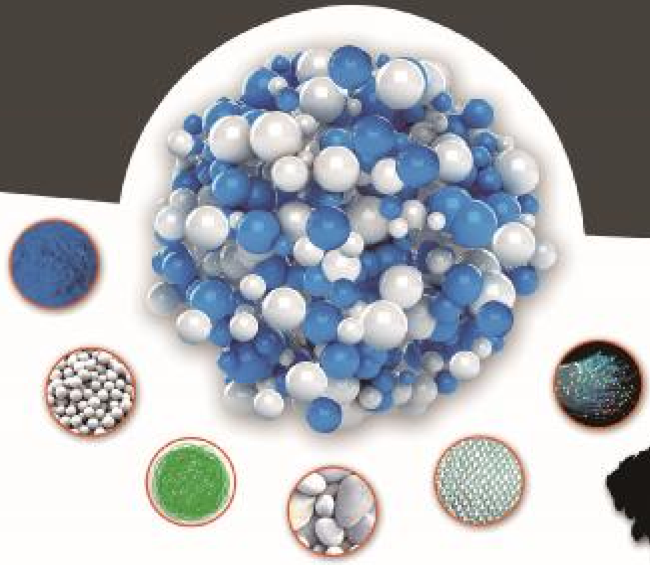
操作手册



北京彼奥德电子有限公司

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物理吸附　真实密度

First of all, thank you for choosing our company's products. Our company's self-developed, manufactured, and marketing products mainly include:

1. Specific surface area and pore size analyzer
2. Temperature programmed chemical adsorption instrument
3. Gas Pycnometer, true density instrument
4. Vapor adsorption instrument
5. Static Volumetric gas adsorption instrument series
6. Static Volumetric high-pressure adsorption instrument series
7. Bubble point method membrane pore size analyzer
8. Laboratory gas distribution instrument series (providing air intake solutions for infrared/mass spectrometry, etc.)
9. Customized series of small-scale catalytic evaluation devices (including VOCs generation and treatment series, SCR denitrification and desulfurization series, etc.)
10. Online mass spectrometer series

Beijing Builder Electronic Technology Co., Ltd. was established on January 9, 2003, specializing in the technical research and development of material characterization instruments. It is a technical service enterprise that integrates project research and development, product production, and testing consulting. Over the course of more than 20 years of development, the company has accumulated a group of high-quality R&D and application technology talents. With strong technical support and personnel infrastructure guarantee, Biotech is able to independently complete the production of products and the research and development and manufacturing of core components. It can provide technical development services beyond the main product scope for scientific research units and enterprises at all levels。

Attention：

This operation manual describes all the functions of the PCA-1200 chemical adsorption instrument, and your product may not have all the functions listed in this manual.

Due to violation of its correct use or clearly defined as foreseeable improper operation, it is not covered by the warranty.

1. The software version number involved in this manual is V2.9.10.12.
2. Before using this product for the first time, please read the operating manual carefully. If you have any questions or suggestions, please call 400-6698981 or send an email to service@ bjbiaode.com .
3. Our company will continuously improve and update the performance and variety of various instruments. Therefore, we reserve the right to make changes to the scope of supply, equipment, and technical specifications.
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Table of Contents

Chapter 1 Specifications

Analysis method:：	Continuous flow programmed heating method
Adsorbed gas：	H_2、O_2、CO、CO_2、NO、SO_2、H_2S、NH_3
Detector：	Gold-plated TCD detector
Test content：	TPD\TPR\TPO\TPS\TPRS Metal dispersion Active metal surface area O_2 storage capacity/H_2 storage capacity……
Analysis temperature：	room temperature ---1000℃
Analysis of Pressure：	ordinary pressure
Safety system：	High precision combustible gas warning
Flow control：	Mass flow controller
Air circuit control system：	High precision 12 in 1 solenoid valve control module
Sampling system：	2 position 6 way valve
Gas input port：	6 ports
Exhaust port：	4 ports
Reactor：	U-shaped bifurcated quartz reactor
Report output：	TXT、PDF
Specifications and dimensions：	L600 x W420 x H700 mm
Power：	AC220V 、500W

Chapter 2 Instrument Schematic Diagram

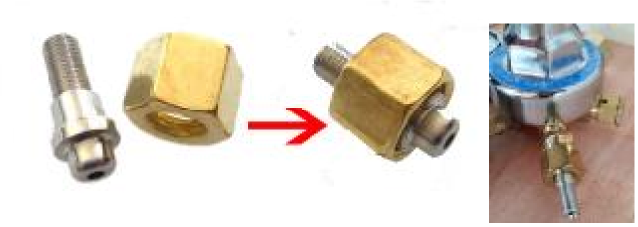
Chapter 3 Basic Structure of Instrument System

- One set of chemical adsorption apparatus host
- One set of analysis computer
- Test gas
- Temperature programmed electric heaterGas circuit connecting pipe

Chapter 4 Installation and Inspection of Instruments

一、Installation and requirements of pressure reducer

1. Assemble the air circuit adapter.



2. Connect the pressure reducer and the gas cylinder, and tighten the nut after wrapping the raw material belt around the pressure reducer interface.

3. The output pressure of the secondary gauge is adjusted to 0.3MPa.

二、Installation of gas cylinder

Install 1 nut and 2 nuts on both ends of each air pipe in turn Φ Seal ring.

Note: During installation, the gas cylinder should be on the right side of the instrument, the host should be close to the window as much as possible, and the exhaust pipe should not be too long.

1. Installation of carrier gas circuit

If the length allows, the intake pipe is bent into spiral shape, which can effectively reduce the baseline run-out caused by unstable output pressure of the pressure reducer.

2. Installation of processing gas circuit

Attention shall be paid to avoid simultaneous access of reactive gases such as hydrogen and oxygen.

3. Installation of pulse gas circuit

4. Installation of exhaust gas path

Attention shall be paid to separation of exhaust air channels. In case of special circumstances, the reference and test can be connected in parallel. The exhaust air and test outlet shall not be connected in parallel to avoid TCD pollution.

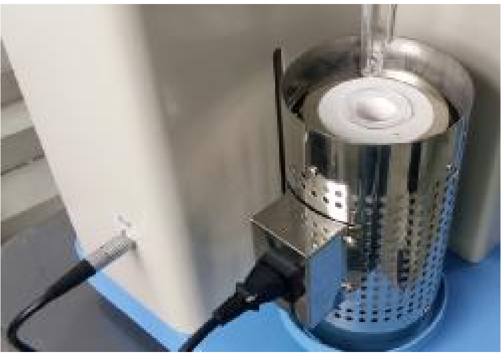
三、Installation and operation of instruments

1. Installation and use of temperature programmed electric furnace

(1) Installation of power line

The interface of the electric furnace is located on the left side of the host, and "point-to-point" is required when inserting the power line of the furnace; When pulling out, just hold the power line interface terminal and pull out.

(2) Installation of electric furnace



Note: Since the quartz tube core on the inner wall of the furnace core is movable, the furnace mouth cannot be downward when the electric furnace is taken out and moved.

2. Installation and use of reactor

(1) Installation of reactor


①


②


③

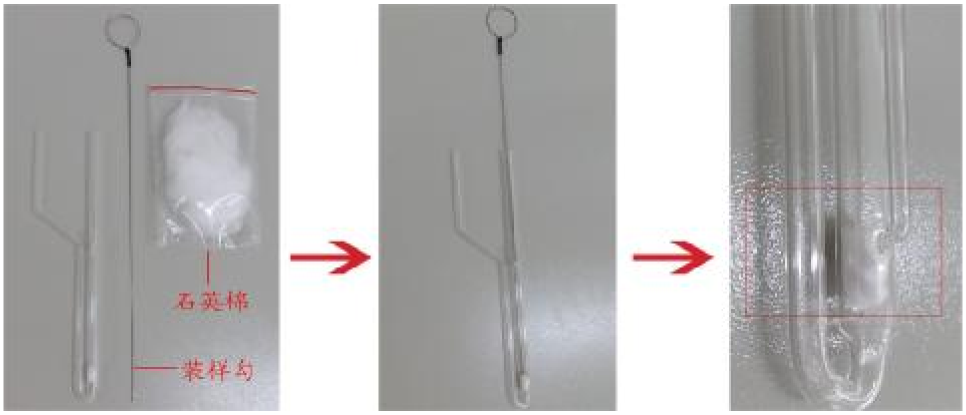

④


⑤


⑥

Note: Keep the reactor vertical to the ground during installation; When tightening the nuts, hold the branch pipes on both sides with one hand and tighten the nuts with the other hand.

(2). Use of reactors



Insert a small amount of quartz wool into the right coarse tube of the reactor, and move the quartz wool to the bottom of the branch tube with a sample hook. The upper end of the quartz wool shall be consistent with the bottom of the branch tube.

PS: the bottom position of branch pipe is the temperature measurement position)

3. Installation and use of cold trap

(1) Impurity removal: mainly used in tpr experiment. Glass cold trap tube is used. Color changing silica gel is added to the glass cold trap tube. Ice water mixture is added to the cold trap tube. It cannot be used in NH3-TPD experiment. Desorpted ammonia will be absorbed by color changing silica gel and desorption peak cannot be obtained.

(2) Cooling: In addition to the tpr experiment, a metal cold trap tube was used to addan ice water mixture to the cold trap.

4. Software and driver installation

(1) Installation of software

Open the installer and double-click the installation. Install according to the operating instructions.

(2) Installation of drive

① Installation of XP/Win7 system driver

Ensure that the data cable between the computer and the analysis host is correctly connected and turned on before installing the driver.

- Find "My Computer", right-click to select Properties, open Device Manager, then find "Universal Serial Bus Controller" and open it, as shown in the following figure.

通用串行总线控制器
Generic USB Hub
Generic USB Hub
Intel(R) 8 Series/C220 Series USB Enhanced Host
Intel(R) 8 Series/C220 Series USB Enhanced Host
USB Composite Device
USB Root Hub

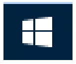
- Find the location where "!" appears and double click to select customized update drive.
- Select the driver "32 bit system driver" or "64 bit system driver" in the installation program to update.

② Installation of Win10 system driver

- Before installing the driver, remove the ban program of win10 system. Operation methods are as follows:

**** Precautions: Do not insert the USB stick in the following steps ****

1. There are three ways to open the window setting:

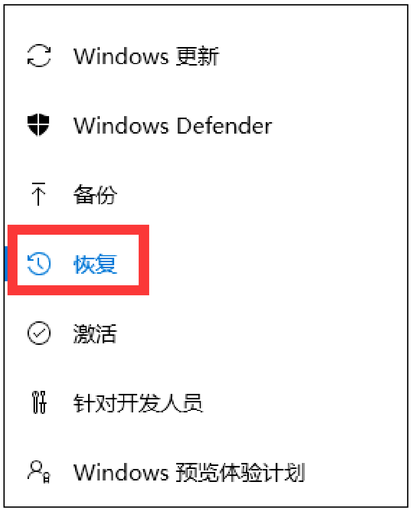
A. Click the "window" button at the bottom left corner " ， Then click "Gear" 

B. Right click the mouse on the desktop, click "Display Settings", and then click "Home Page"

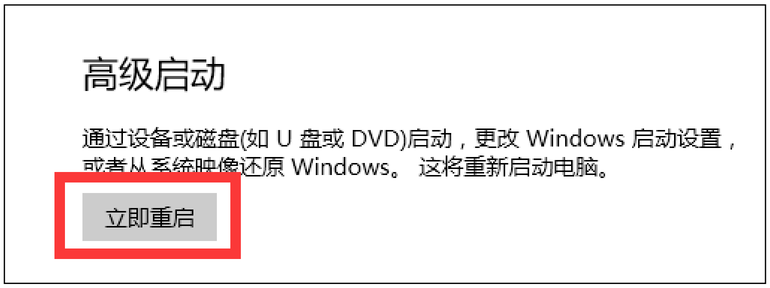
C. Click on the Notification to locate and enter "All Settings".

2. Click "Update and Security"

3. Click "Recover"



4. Click "Start Now" under "Advanced Startup", and the computer will restart after clicking.



高级启动

通过设备或磁盘(如 U 盘或 DVD)启动，更改 Windows 启动设置，或者从系统映像还原 Windows。 这将重新启动电脑。

5. Select "Troubleshooting" after restarting

6. Select "Advanced Options"

疑难解答

重置此电脑

让你选择保留或删除你的文件，然后重新安装 Windows。

高级选项

7、Select "Start setting"”

高级选项

系统还原

命令提示符

系统映像恢复

启动设置

启动修复

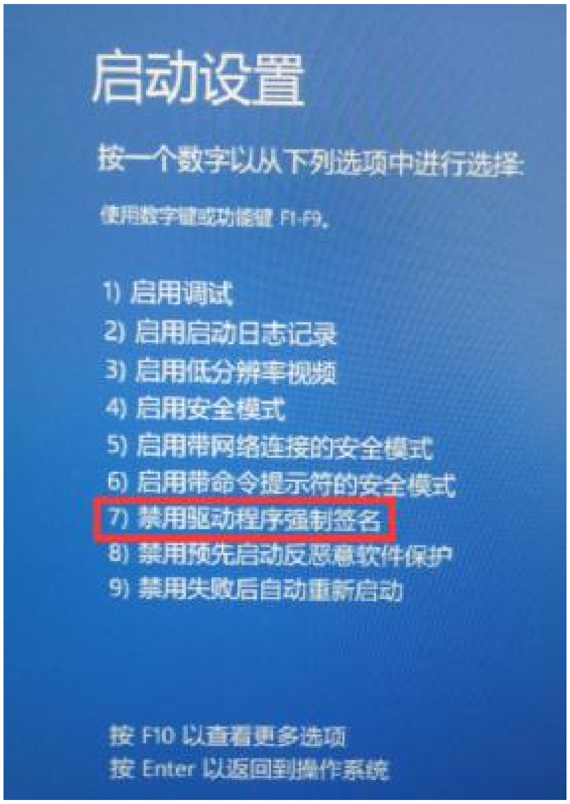
回退到以前的版本

8. Click "Restart" and the computer will restart.

启动设置

重启以更改 Windows 选项，例如:

9. After the computer is started, press "7" to complete the setting.



启动设置

按一个数字以从下列选项中进行选择:

使用数字键或功能键 F1-F9。

1) 启用调试
2) 启用启动日志记录
3) 启用低分辨率视频
4) 启用安全模式
5) 启用带网络连接的安全模式
6) 启用带命令提示符的安全模式
7) 禁用驱动程序强制签名
8) 禁用预先启动反恶意软件保护
9) 禁用失败后自动重新启动

按 F10 以查看更多选项
按 Enter 以返回到操作系统

Install the driver according to the installation method of XP/Win7 system driver after setting.

Chapter 5 Use of Instruments

一、Selection of test gas

1. When selecting carrier gas, try to use two component gases with large difference in thermal conductivity (the thermal conductivity of common gases is shown in the following table) to avoid TCD unable to identify the concentration change of components.

Gas type	thermal conductivity
Hydrogen (H2)	0.163
Helium (He)	0.144
Argon (Ar)	0.0173
Neon (Ne)	0.0455

Oxygen (O2)	0.0240
Nitrogen (N2)	0.0228
Ammonia (NH3)	0.0215
AIR	0.0233
Carbon monoxide (CO)	0.0226
Carbon dioxide (CO2)	0.0137
Methane (CH4)	0.0300
Ethane (C2H6)	0.0180
Propane (C3H8)	0.0148
Ethylene (C2H4)	0.0164
Acetylene (C2H2)	0.0184

2. Use of different test gases (note that 99.999% purity is required for all of the following test gases)

① NH3-TPD experiment: argon or nitrogen, ammonia
② CO2-TPD experiment: CO2, helium
③ O2-TPD experiment: oxygen and helium
④ H2-TPR test: argon or nitrogen, hydrogen/argon mixture (hydrogen content 5% - 10%)
⑤ O2-TPO experiment: helium, helium/oxygen mixture (oxygen content 5% - 10%)
⑥ Metal dispersion test: hydrogen (if the metal load is very low, it is advisable to use low concentration hydrogen), oxygen, argon or nitrogen
⑦ Oxygen storage: helium, oxygen and hydrogen

Note: Please prepare all gases, and prepare a matched pressure reducer according to the nature of the gas. The output pressure can be adjusted to 0.3~0.5MPa.

二、Preconditioning of sample before machine analysis

Since the state of the sample before analysis cannot be controlled, the sample may contain a lot of moisture, organic matter or corrosive substances inside. Before analysis, in order to ensure that the impurities in the analysis sample do not pollute the instrument, damage or corrode the instrument pipeline, pretreatment is usually carried out before online analysis.

三、Determination of sample analysis amount

For optimum accuracy and repeatability, you should note that:

1. Use the equivalent sample size for each analysis (especially for comparison between samples).
2. The sample is well dispersed in the pipe, so the sample shall not be stacked on one side of the pipe, or the pipe wall is stained with many samples.
3. Ensure that the particle distribution of the sample is unchanged (the large particle distribution and small particle distribution of the same material will affect the reaction speed). For samples with wide range distribution, pay attention to representativeness of sampling.
4. Recommended sample weight is between 20 mg and 2 g. The sample shall be within about 20 mm of the bottom of the sample tube. When determining the sample size, the percentage content of active metal shall be taken into account, and the sample size shall be increased for the sample with low content. Powder samples are taken from a long neck funnel and added to the bottom of the sample tube. Samples of large particles shall be added with nippers.

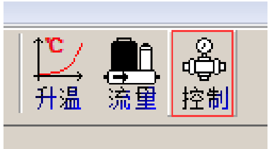
四、Installation of sample tube

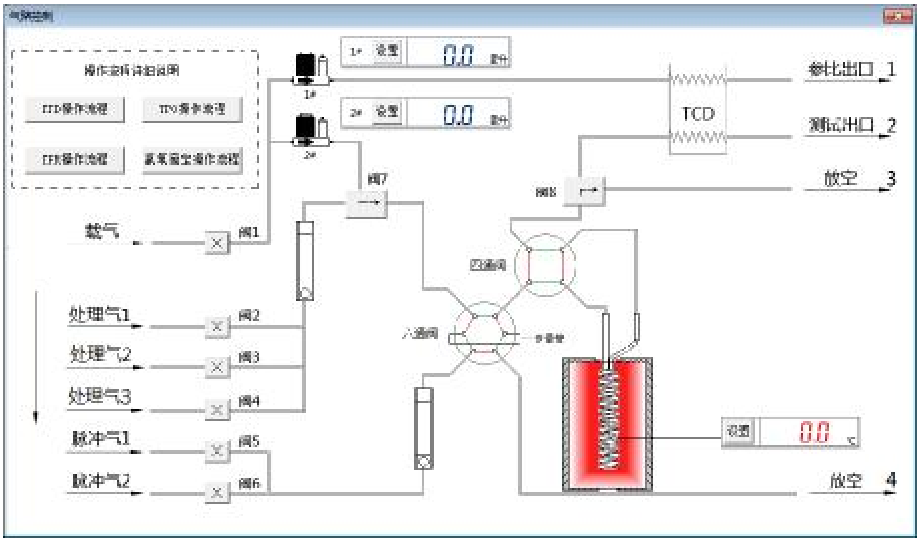
1. It is better to wear gloves to hold the quartz tube, because the salt on the hand will reduce the melting point of the quartz tube, and the grease on the skin will stick to the quartz tube and damage the quartz tube during heating.
2. Respectively install two sets of large and small fixed seal ferrules on the thick and thin sample tube. Be careful not to let the ferrule slide down the tube wall from the upper part and break the sample tube.
3. Install the O-ring seal at the opening of the sample tube.
4. Secure the sample tube to the analysis port with the shrink nut.

五、Gas circuit control

The air circuit is controlled by the software, and the corresponding numbered solenoid valve is opened and closed according to the analysis steps.

Or directly click the "Control" button

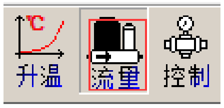


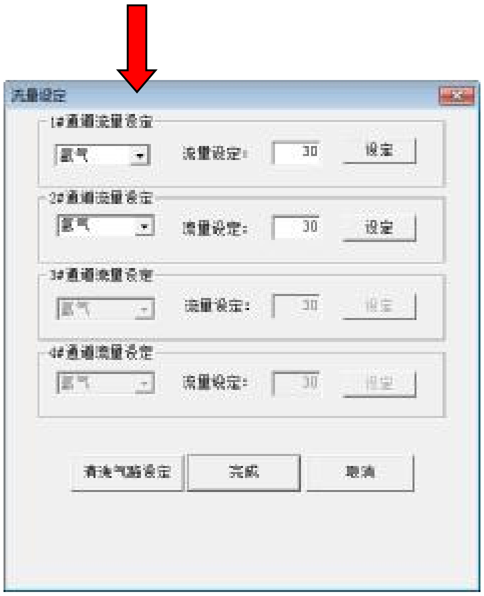


六、Flow setting

Flow regulation of test gas; Select the gas type in the two channels and set the flow. Click the "Finish" button to end the flow setting.

or directly click on the "Gas flow rate" button

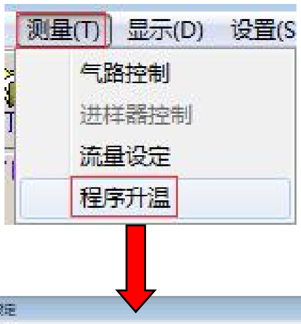




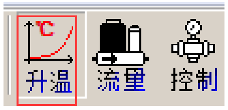
七、Temperature Programmed Heating, setting for test process

Set the programmed temperature rise according to the experimental conditions. After setting the temperature and temperature rise rate, click "Add temperature control section" to complete the setting, and click "Start programmed temperature rise" to complete the temperature rise control.

Note: Make sure that the thermocouple and the programmed temperature rise electric furnace have entered the operation position before clicking the start of programmed temperature rise。



or directly click "Rise" button



程序升温：第一段

开始程序升温

温度设定：300 ℃(1-1200)

升温速率：5 ℃/Min(1-30)

恒温时间：30 Min(1-300)

加入温控段

段号	升温设定(℃)	升温速率(℃/Min)	恒温时间(Min)
1	300	5	30
2	600	10	30
3	900	10	30

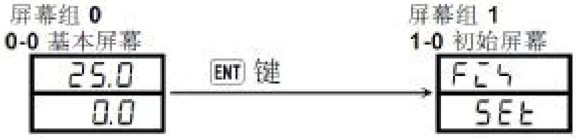
八、Instructions for TCD Temperature Control Meter

1. Set the temperature sensor type and temperature unit (degrees Celsius or degrees Fahrenheit)

On the first page of the initial 0 screen group (the default window displayed after power on), long press ⟲ and hold for three seconds to enter screen group 4.

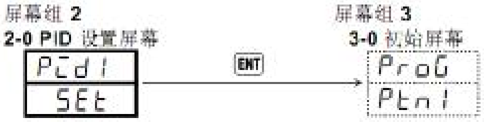
- press ⟲ and switch to rAnG (select temperature sensor type), select 05 (K-type thermocouple)，press ENT to confirm.
- Press ⟲ to switch to Unit (select temperature measurement unit)，press ENT to confirm. “C”is degrees Celsius, “F” is degrees Fahrenheit, and the initial value is “C”.
- Exit screen group 4, hold down ⟲ until SEt displayed, then hold down ⟲ for three seconds to exit screen group 4 and return to initial screen group 0.

2. Set manual temperature rise control or programmed temperature rise control



- Press ENT on the basic screen of screen group 0 to switch to "1-0 initial screen" of screen group 1.
- FIX control ON/OFF setting screen.
- Initial Setup：ON
- set an option：ON，OFF
- ON：Manual constant temperature rise control；OFF：Programmed temperature control
- Exit screen group 1，press ⟲ to switch to FIX SEt 1-0 initial screen，then press ENT to switch to the screen group 0-0 initial screen.

3、Program temperature setting



- Switch to the initial screen of screen group 3 (program control) by pressing ENT at the "2-0 Initial Screen" button in screen group 2.
- Press ⟲ to switch to StEP SEt, press ▲ or ▼ to choose StEP 1.
- Press ⟲ to switch to S.01 0.0, This code is used to set the temperature for heating up，press ▲ to set the temperature，press ENT to confirm.
- Press ⟲ to switch to t.01 0.00, This code is used to set the heating time (if the temperature rises to 500 degrees per minute at 10 degrees, the time value of this code needs to be set to 50 minutes)，press ▲ to set the time you need，press ENT to confirm.
- Press ⟲ to switch back to StEP 1, press ▲ or ▼ to switch to StEP SEt code，then press ⟲ to switch back ProG PtnI 初始屏幕(曲线1), than press ENT to switch back screen group 0-0.

Chapter 6 Experimental Procedures

一、Catalyst acidity analysis（NH_3-TPD）

（一） Preparation before experiment

1、Connect the carrier gas interface to N_2 and the processing gas 2 interface to NH_3.

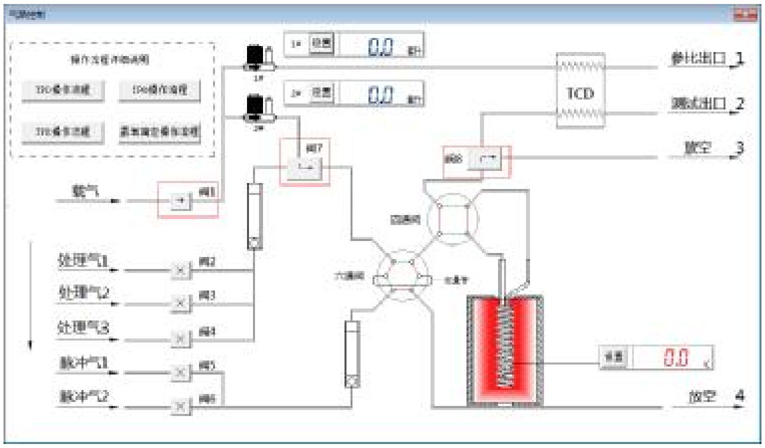
2、Fill the bed layer, load the sample into the reactor, approximately 0.05-0.5g (experimental temperature<600 ℃, use a glass reactor;<1000 ℃, use a quartz reactor), and connect to the instrument interface.

（二） Conduct experiments

1、Remove residual gas from the gas path.

(1) Open the host, software, and N2 cylinder valve (adjust the output pressure to 0.3-0.4 MPa).

(2) Adjusting the air circuit: software → measurement → air circuit control → valve 1 → valve 7 ( ) → valve 8 ( ) switches to venting → closes the window.



(3) Adjust the flow rate: software → measurement → flow setting → 2 # set to 30ml/min → complete and close the window.

- Here, channels 1 # and 2 # refer to the instrument carrier gas channel (1 # is the reference port flow rate; 2 # is the test port channel).

Note: When setting the flow rate, attention should be paid to selecting the corresponding gas to complete the coefficient conversion of the flowmeter. For example, when using a mixed gas, select a gas with a large proportion of components for coefficient conversion.


流量设定

1#通道流量设定
氮气 流量设定: 30 设定

2#通道流量设定
氮气 流量设定: 30 设定

3#通道流量设定
氮气 流量设定: 30 设定

4#通道流量设定
氮气 流量设定: 30 设定

(4) Purge the sample in an inert gas environment at room temperature for at least 10 minutes.

2、Programmed heating pretreatment (dehydration)

(1) Raise the furnace and insert the thermocouple into the bottom of the reactor branch pipe

(2) Setting conditions: 1 to 10 stages of programmed heating can be set according to experimental conditions. Relevant parameters can be set according to experimental conditions: measurement → programmed heating → setting temperature upper limit, heating rate, and constant temperature time → adding temperature control section → clicking to start the program → closing the interface.

程序升温：第一段

温度设定：300 ℃(1-1200)

升温速率：5 ℃/Min(1-30)

恒温时间：30 Min(1-300)

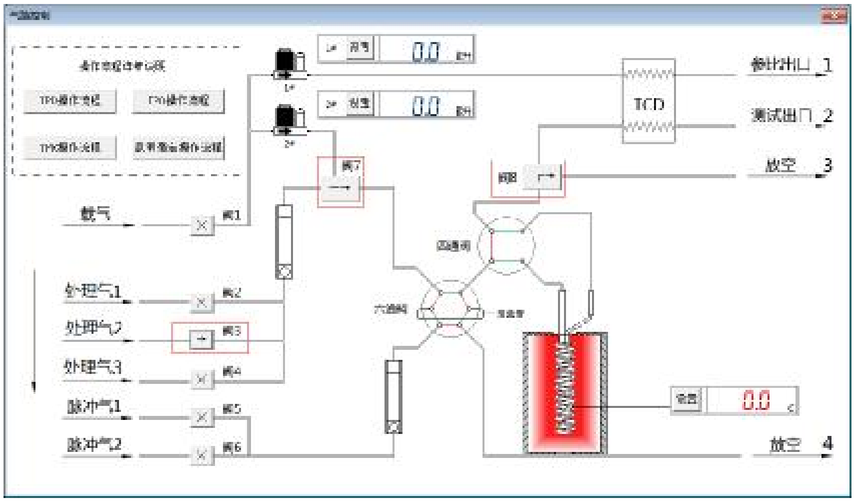
段号	升温设定(℃)	升温速率(℃/Min)	恒温时间(Min)
1	300	5	30
2	600	10	30
3	900	10	30

(3) After the program heating program is completed, when the furnace temperature drops below 200 ℃, lower the furnace (to avoid thermocouple damage), continue to use N2 for purging, and proceed with the next operation after the temperature of the sample position returns to room temperature (generally, the furnace body can be cooled to below 50 ℃ within 30-40 minutes for strong cooling systems) .

3、Saturated adsorption NH_3

(1) Open the NH_3 cylinder valve

(2) Adjust the air circuit: flow rate → air circuit control → valve 3 → valve 7 (→) → valve 8 (↱) switch to vent and turn on the rotameter.



(3) Adjusting the flow rate: Adjust the rotary flowmeter on the instrument panel to 40ml/min.

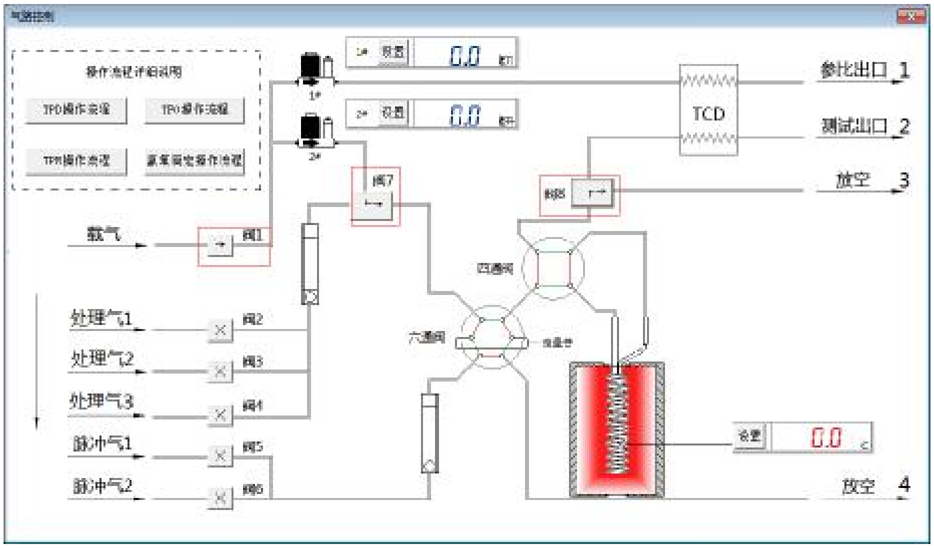
(4) The adsorption temperature of NH3 is generally between 50-100 ℃, and the adsorption time is 15-20 minutes.

(5) Removing physically adsorbed NH_3

- At a certain temperature (usually NH3 adsorption temperature), use N2 for purging, and the steps are as follows：

① Open the N_2 gas cylinder valve (adjust the output pressure to 0.3-0.4 MPa)

② Adjusting the air circuit: software → measurement → air circuit control → valve 1 → valve 7 (└▸) → valve 8 (┌▸) switches to venting → closes the window



③ Adjust the flow rate: software → measurement → flow setting → 2 # set to 30ml/min → complete and close the window

Here, channels 1 # and 2 # refer to the instrument carrier gas channel (1 # is the reference port flow rate; 2 # is the test port channel)

Note: When setting the flow rate, attention should be paid to selecting the corresponding gas to complete the coefficient conversion of the flowmeter. For example, when using a mixed gas, select a gas with a large proportion of components for coefficient conversion.

1#通道流量设定
氮气 流量设定：30

2#通道流量设定
氮气 流量设定：30

3#通道流量设定
氩气 流量设定：30

4#通道流量设定
氩气 流量设定：30

④ Setting conditions: 1 to 10 stages of programmed temperature setting can be carried out, and relevant parameters can be set according to experimental conditions: measurement → programmed temperature rise → setting temperature upper limit, heating rate, and constant temperature time → adding temperature control section → clicking on start program → closing interface (in the previous step, a longer constant temperature time can be set, and after reaching the adsorption time, the gas path can be switched to complete the physical adsorption of NH3 removal)

程序升温：第一段

温度设定：300 ℃(1-1200)

升温速率：5 ℃/Min(1-30)

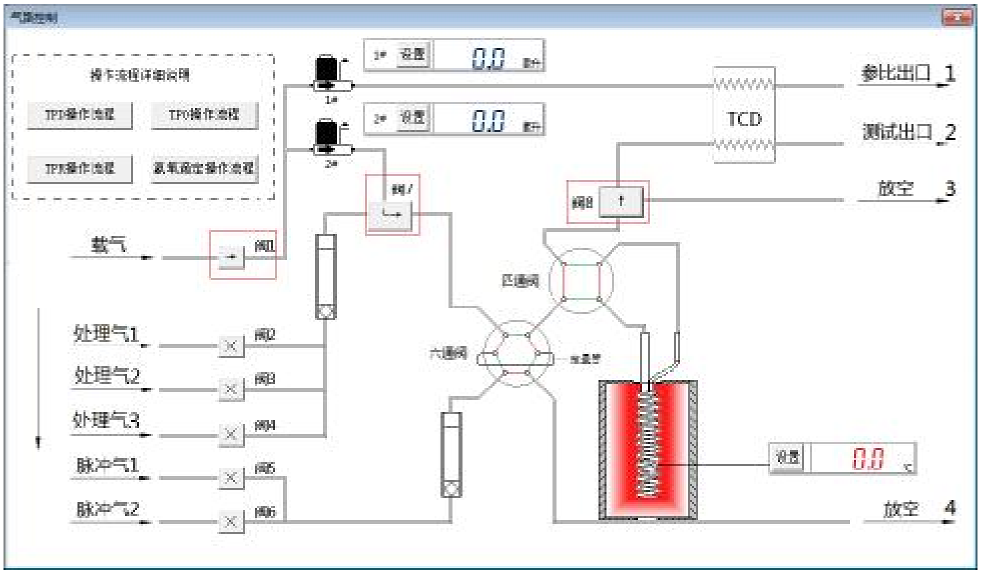
恒温时间：30 Min(1-300)

段号	升温设定(℃)	升温速率(℃/Min)	恒温时间(Min)
1	300	5	30
2	600	10	30
3	900	10	30

4、**Temperature Programmed Desorption**

(1) Open the N_2 gas cylinder valve (adjust the output pressure to 0.3-0.4 MPa)

(2) Adjusting the air circuit: measurement → air circuit control → valve 1 → valve 7 (↳) → valve 8 (↑) switches to TCD → closes the window → opens TCD.



(3) Adjust the flow rate: Measure → Set the flow rate → Set # 1 to 30ml/min → Set # 2 to 30ml/min → Complete and close the window

Here, channels 1 # and 2 # refer to the instrument carrier gas channel (1 # is the reference port flow rate; 2 # is the test port channel)

Note: When setting the flow rate, attention should be paid to selecting the corresponding gas to complete the coefficient conversion of the flowmeter. For example, when using a mixed gas, select a gas with a large proportion of components for coefficient conversion.

(4) Adjust the polarity according to the TCD polarity, open the TCD, and wait for the baseline to level out (multiple zeros are required during the stabilization process, and wait for the voltage variation range to be ± 20 μ v. Raise the furnace to the designated position (due to the previous heating operation, there may be residual temperature in the furnace body. Generally, the forced cooling system requires 30-40 minutes for the furnace body to cool down to below 50 ℃. After the temperature stabilizes, adjust the baseline to zero for the next step.)

(5) Setting conditions: Measurement → Program heating → Set temperature upper limit, heating rate, and constant temperature time → Add temperature control section → Click to start the program → Close the interface.

程序升温：第一段
温度设定：300 ℃(1-1200)
升温速率：5 ℃/Min(1-30)
恒温时间：30 Min(1-300)

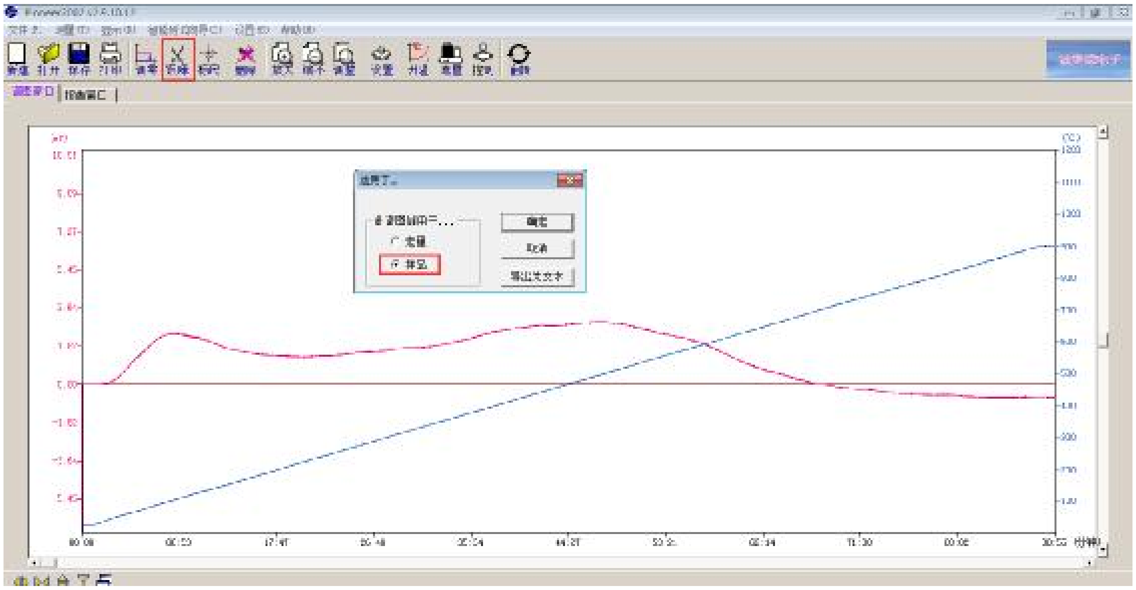
段号	升温设定(℃)	升温速率(℃/Min)	恒温时间(Min)
1	300	5	30
2	600	10	30
3	900	10	30

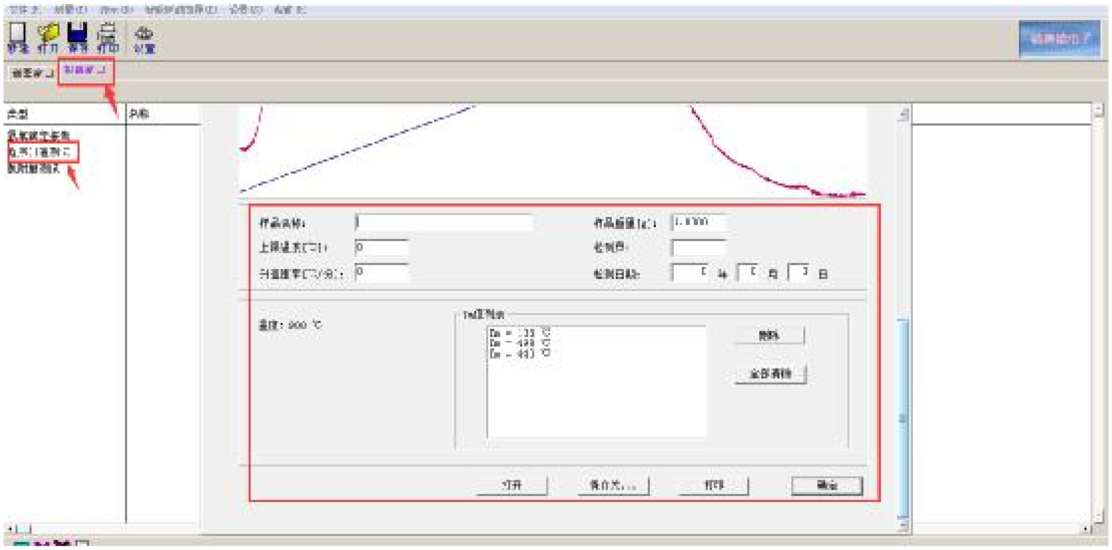
（三） Experimental completion

After the program is completed, save the data, close the TCD thermal conductivity cell, turn off the gas, turn off the chemical adsorption instrument host, and recycle or dispose of the sample.

（四） Data processing

Software → Click on the "peak recognition" button (select the "spectrum" on the software interface) → Sample → Confirm, select the "report window" button, select "program temperature rise test" to open the spectrum, and fill in the basic parameters.





二、Temperature Programmed Reduction (H2-TPR)

（一） Preparation before experiment

1. Connect the carrier gas interface to Ar/H_2 or N_2/H_2 mixture (H25% -10%); Process gas 1 interface connected to N_2 or Ar

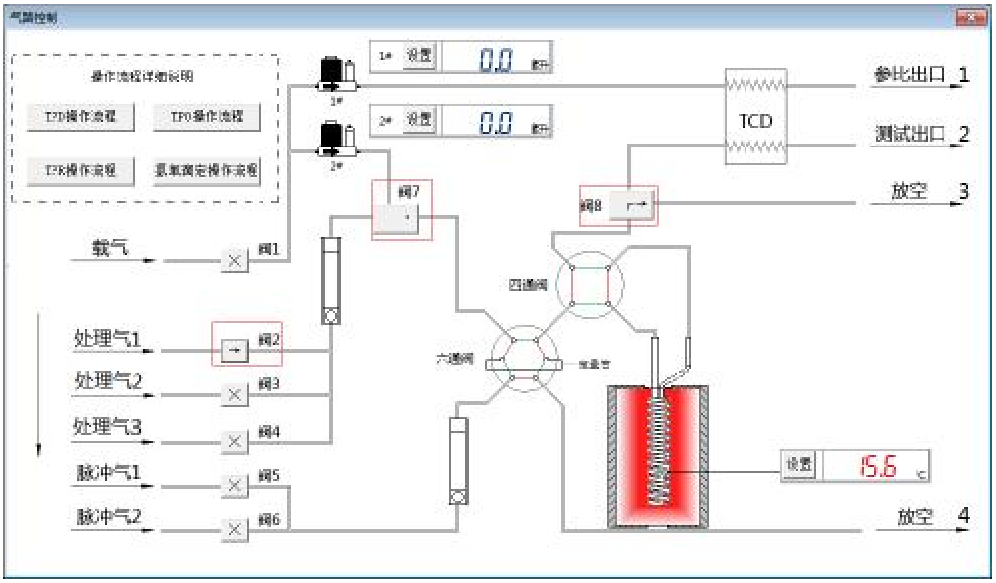
2. Fill the bed layer, load the sample into the reactor, approximately 0.05-0.5g (experimental temperature<600 ℃, use a glass reactor;<1000 ℃, use a quartz reactor), and connect to the instrument interface.

（二） Conduct experiment

1. Remove residual gas from the gas path

(1) Open the host, software, and N2 cylinder valve (adjust the output pressure to 0.3-0.4 MPa)

(2) Adjust the air circuit: software → measurement → air circuit control → valve 2 → valve 7 (⟶) → valve 8 (↱) switch to vent → close the window



(3) Adjusting the flow rate: Adjust the rotary flowmeter on the panel to 40ml/min

(4) Purge the sample in the normal temperature environment for at least 10 minutes.

2、Programmed heating pretreatment (dehydration)

(1) Lift the furnace and insert the thermocouple into the bottom of the reactor branch pipe

(2) Setting conditions: 1 to 10 stages of programmed heating can be set according to experimental conditions. Relevant parameters can be set according to experimental conditions: measurement → programmed heating → setting temperature upper limit, heating rate, and constant temperature time → adding temperature control section → clicking on start program → closing interface

程序升温：第一段

温度设定：300 ℃(1-1200)

升温速率：5 ℃/Min(1-30)

恒温时间：30 Min(1-300)

段号	升温设定(℃)	升温速率(℃/Min)	恒温时间(Min)
1	300	5	30
2	600	10	30
3	900	10	30

(3) After the program heating program is completed, when the furnace temperature drops below 200 ℃, lower the furnace (to avoid thermocouple damage), continue to use N_2 for purging, and proceed to the next step after the temperature of the sample location returns to room temperature.

Optional steps: The sample needs to be reduced according to its condition. The steps are as follows

(1) Connect O_2 at the processing gas 2 interface, open the O_2 cylinder valve (adjust the output pressure to 0.3-0.4 MPa)

(2) Adjust the air circuit: software → measurement → air circuit control → valve 3 → valve 7 (→) → valve 8 (┌→) switch to vent → close the window

(3) Adjust the flow rate: Adjust the rotary flowmeter on the panel to 40ml/min

(4) Lift the furnace and insert the thermocouple into the bottom of the reactor branch pipe

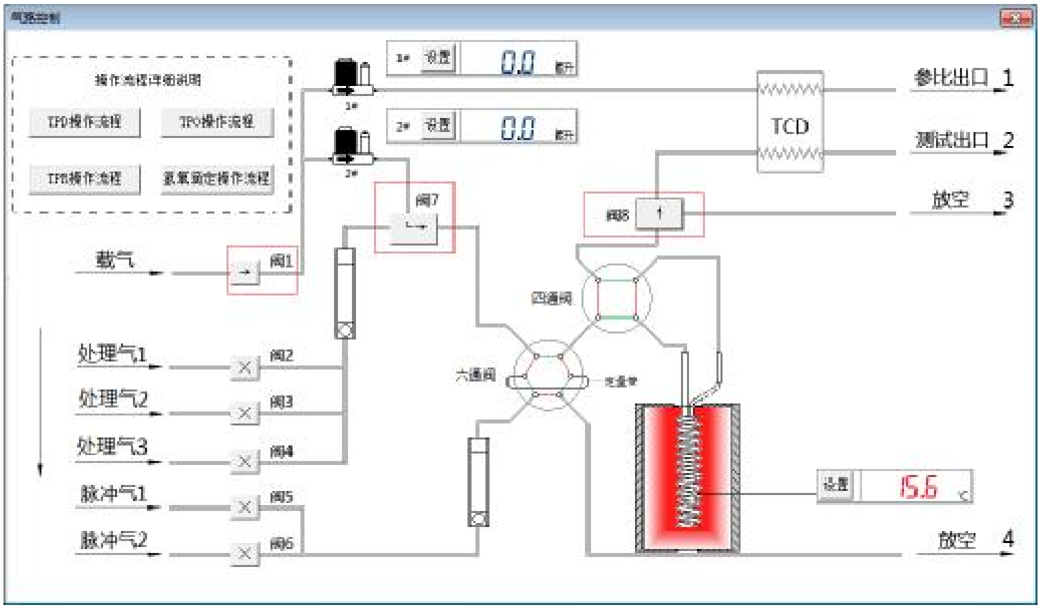
(5) Setting conditions: 1 to 10 stages of programmed heating can be set according to experimental conditions. Relevant parameters can be set according to experimental conditions: measurement → programmed heating → setting temperature upper limit, heating rate, and constant temperature time → adding temperature control section → clicking on start program → closing interface

(6) After the temperature program is completed, when the furnace temperature drops below 200 ℃, lower the furnace (to avoid thermocouple damage) and continue to use O_2 for purging. After the temperature of the sample position returns to room temperature, switch to treatment gas 1. After using N_2 to purge the gas path for 10 minutes, the next step can be taken

3、**Temperature Programmed Reduction, TPR**

(1) Open the Ar/H2 mixed gas cylinder valve (adjust the output pressure to 0.3-0.4 MPa)

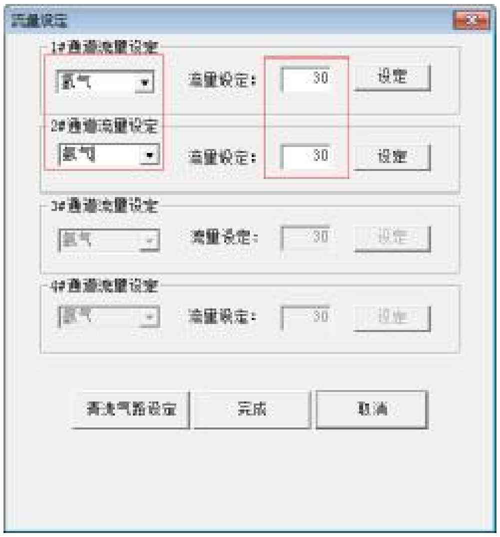
(2) Adjust the air circuit: measurement → air circuit control → valve 1 → valve 7 (└▸) → valve 8 (↑) switches to TCD → closes the window → opens TCD



(3) Adjust the flow rate: Measure → Set the flow rate → Set # 1 to 30ml/min → Set # 2 to 30ml/min → Complete and close the window

Here, channels 1 # and 2 # refer to the instrument carrier gas channel (1 # is the reference port flow rate; 2 # is the test port channel)

Note: When setting the flow rate, attention should be paid to selecting the corresponding gas to complete the coefficient conversion of the flowmeter. For example, when using a mixed gas, select a gas with a large proportion of components for coefficient conversion.



流量设定

1#通道流量设定
氦气
流量设定：30

2#通道流量设定
氦气
流量设定：30

3#通道流量设定
氦气
流量设定：30

4#通道流量设定
氦气
流量设定：30

(4) Adjust the polarity according to the TCD polarity, open the TCD, and wait for the baseline to level out (multiple zeros are required during the stabilization process, and wait for the voltage variation range to be ± 20 μ v. Raise the furnace to the designated position (due to the previous heating operation, there may be residual temperature in the furnace body. Generally, the forced cooling system requires 30-40 minutes for the furnace body to cool down to below 50 ℃. After the temperature stabilizes, adjust the baseline to zero for the next step)

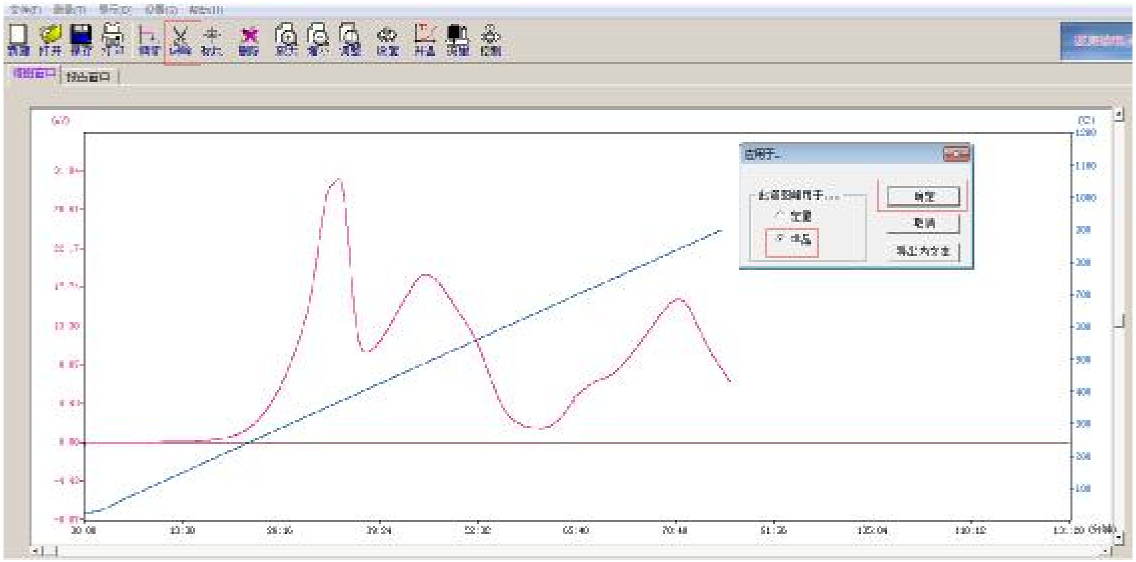
(5) Setting conditions: Measurement → Program heating → Set temperature upper limit, heating rate, and constant temperature time → Add temperature control section → Click to start the program → Close the interface

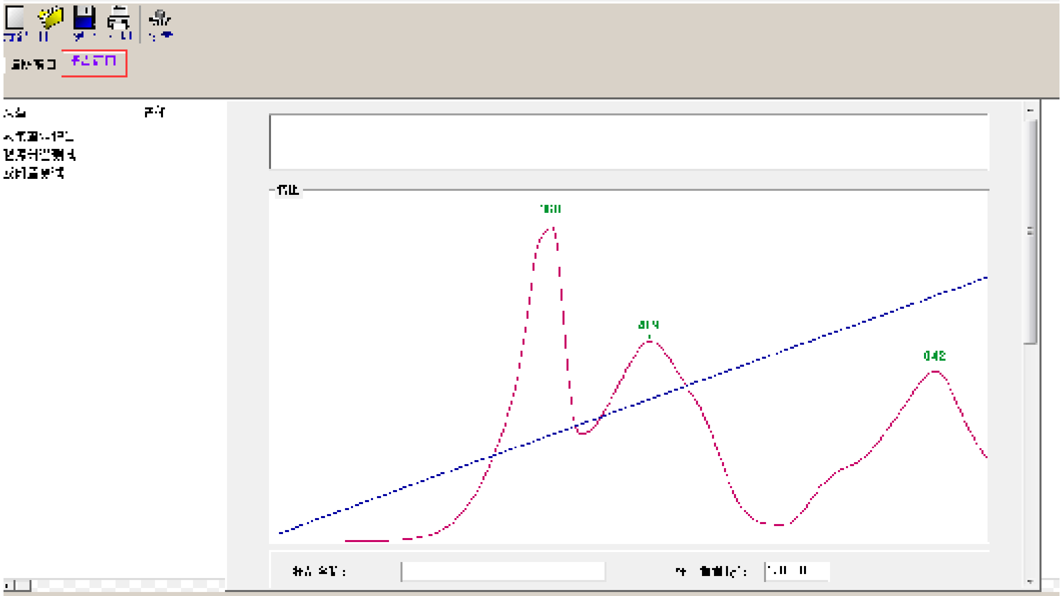
(三) **Experimental completion**

After the program is completed, save the data, close the TCD thermal conductivity cell, turn off the gas, turn off the chemical adsorption instrument host, and recycle or dispose of the sample

（四） **Data processing**

Software → Click on the "peak recognition" button (select the "spectrum" on the software interface) → Sample → Confirm, select the "report window" button, select "program temperature rise test", and fill in the basic parameters.





三、Temperature Programmed Oxidation（O_2-TPO）

（一） Preparation before experiment

1. Connect the carrier gas interface to the He/O2 mixture (02 is 5% -10%); Connect the processing gas 1 interface to N2 or Ar,

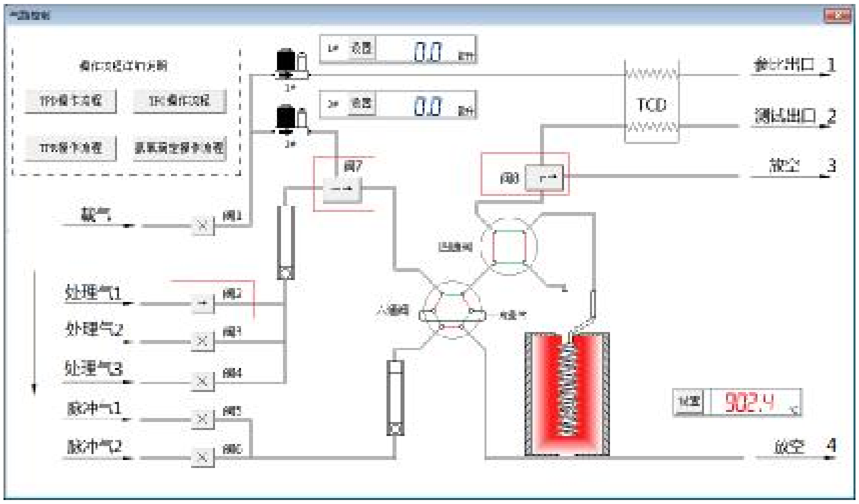
2. Fill the bed layer, load the sample into the reactor, approximately 0.05-0.5g (experimental temperature<600 ℃, use a glass reactor;<1000 ℃, use a quartz reactor), and connect to the instrument interface

（二） Conduct experiment

1、Remove residual gas from the gas path

(1) Open the host, software, and N2 cylinder valve (adjust the output pressure to 0.3-0.4 MPa)

(2) Adjust the air circuit: software → measurement → air circuit control → valve 2 → valve 7 (⟶) → valve 8 (┌→) switch to vent → close the window.



(3) Adjust the flow rate: Adjust the rotary flowmeter on the panel to 40ml/min

(4) Purge the sample at room temperature for at least 10 minutes.

2、Programmed heating pretreatment (dehydration)

(1) Lift the furnace and insert the thermocouple into the bottom of the reactor branch pipe

(2) Setting conditions: 1 to 10 stages of programmed heating can be set according to experimental conditions. Relevant parameters can be set according to experimental conditions: measurement → programmed heating → setting temperature upper limit, heating rate, and constant temperature time → adding temperature control section → clicking on start program → closing interface

段号	升温设定(℃)	升温速率(℃/Min)	恒温时间(Min)
1	300	5	30
2	600	10	30
3	900	10	30

(3) After the program heating program is completed, when the furnace temperature drops below 200 ℃, lower the furnace (to avoid thermocouple damage), continue to use N2 for purging, and proceed with the next operation after the temperature of the sample location returns to room temperature (generally, the furnace body can be cooled to below 50 ℃ within 30-40 minutes for strong cooling systems)

Optional steps: The sample needs to be reduced according to its condition. The steps are as follows

(1) Connect H2 at the processing gas 2 interface, open the H2 cylinder valve (adjust the output pressure to 0.3-0.4 MPa)

(2) Adjust the air circuit: software → measurement → air circuit control → valve 3 → valve 7 (⟶) → valve 8 (┌➔) switch to vent → close the window

(3) Adjust the flow rate: Adjust the rotary flowmeter on the panel to 40ml/min

(4) Lift the furnace and insert the thermocouple into the bottom of the reactor branch pipe

(5) Setting conditions: 1 to 10 stages of programmed heating can be set according to experimental conditions. Relevant parameters can be set according to experimental conditions: measurement → programmed heating → setting temperature upper limit, heating rate, and constant temperature time → adding temperature control section → clicking on start program → closing interface

(6) After the program heating program is completed, when the furnace temperature drops below 200 ℃, lower the furnace (to avoid thermocouple damage), continue to use H2 for purging, and after the temperature of the sample position returns to room temperature, switch to treatment gas 1. After using N2 to purge the gas path for 10 minutes, the next step can be taken

3、Temperature Programmed Oxidation

(1) Open the He/O2 mixed gas cylinder valve (adjust the output pressure to 0.3-0.4 MPa)

(2) Adjust the air circuit: measurement → air circuit control → valve 1 → valve 7 (↳) → valve 8 (↑) switches to TCD → closes the window → opens TCD

(3) Adjust the flow rate: Measure → Set the flow rate → Set # 1 to 30ml/min → Set # 2 to 30ml/min → Complete and close the window

Here, channels 1 # and 2 # refer to the instrument carrier gas channel (1 # is the reference port flow rate; 2 # is the test port channel)

Note: When setting the flow rate, attention should be paid to selecting the corresponding gas to complete the coefficient conversion of the flowmeter. For example, when using a mixed gas, select a gas with a large proportion of components for coefficient conversion.

(4) Adjust the polarity according to the TCD polarity, open the TCD, and wait for the baseline to level out (multiple zeros are required during the stabilization process, and wait for the voltage variation range to be ± 20 μ v) Raise the furnace to the designated position (due to the previous heating operation, there may be residual temperature in the furnace body. Generally, the forced cooling system requires 30-40 minutes for the furnace body to cool down to below 50 ℃. After the temperature stabilizes, adjust the baseline to zero and proceed to the next step)

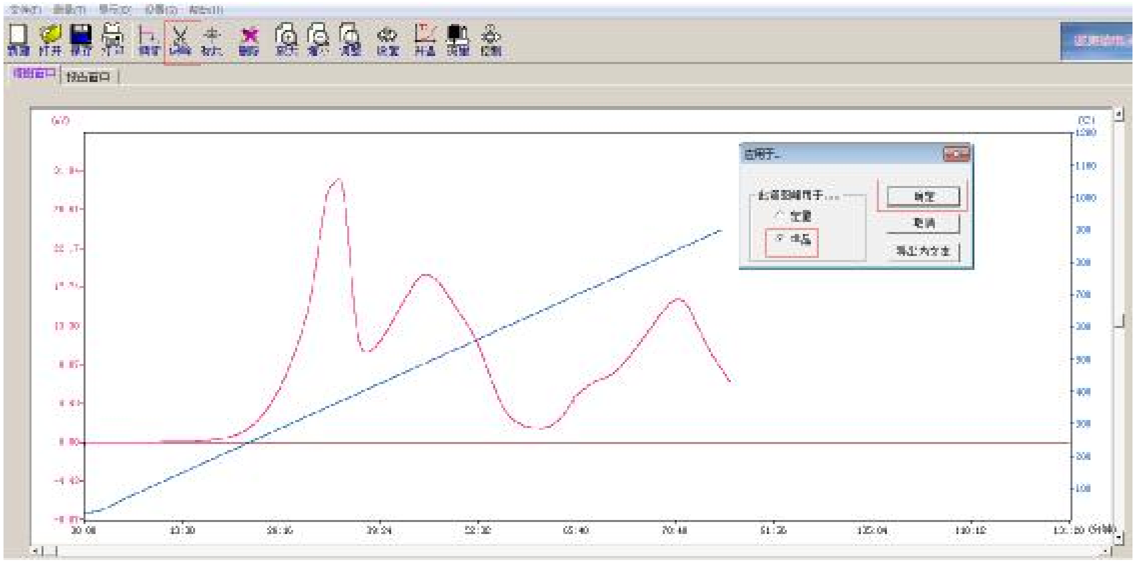
(5) Setting conditions: Measurement → Program heating → Set temperature upper limit, heating rate, and constant temperature time → Add temperature control section → Click to start the program → Close the interface

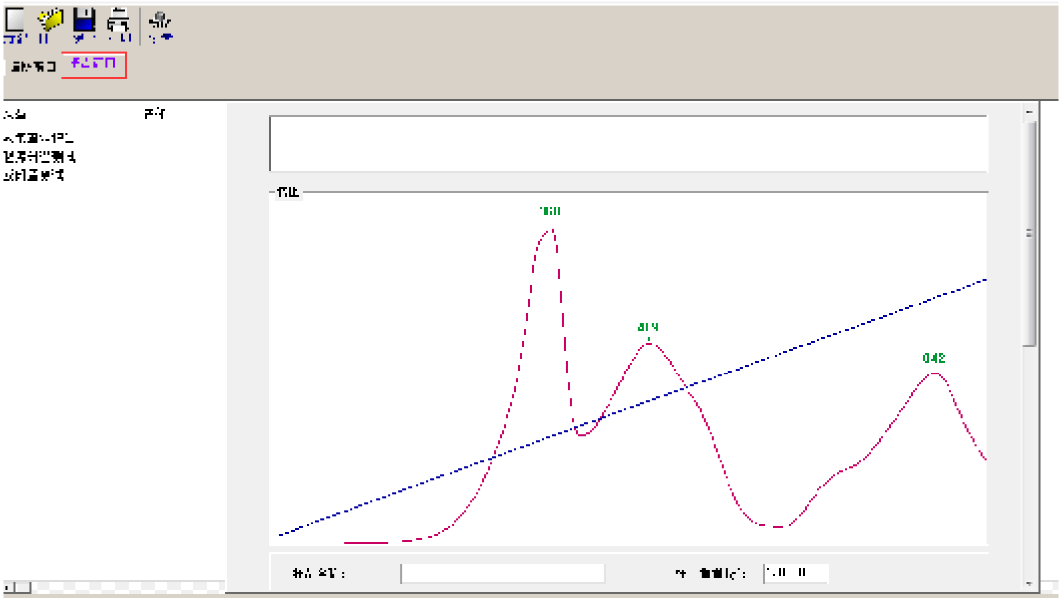
（三） Experimental completion

After the program is completed, save the data, close the TCD thermal conductivity cell, turn off the gas, turn off the chemical adsorption instrument host, and recycle or dispose of the sample

（四） Data processing

Software → Click on the "peak recognition" button (select the "spectrum" on the software interface) → Sample → Confirm, select the "report window" button, select "program temperature rise test", and fill in the basic parameters.





四、Pulse H_2-O_2 titration

（一） Preparation before experiment

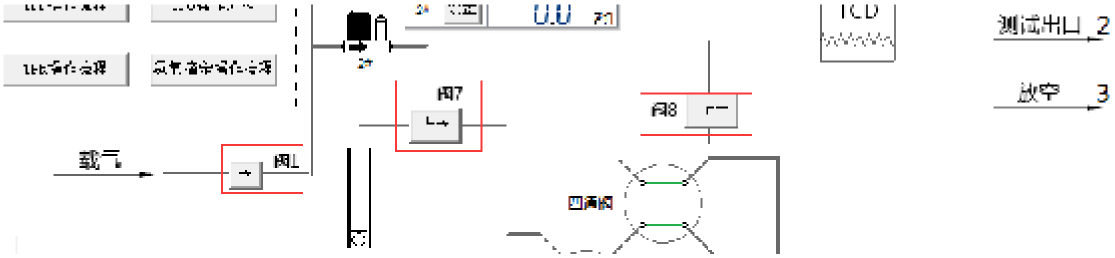
1. Connect the carrier gas interface to Ar; Process gas 1 interface connected to O_2; Connect the processing gas 2 interface to H_2; Pulse gas 1 interface connected to H_2
2. Fill the bed layer, load the sample into the reactor, approximately 0.05-0.5g (experimental temperature<600 ℃, use a glass reactor;<1000 ℃, use a quartz reactor), and connect to the instrument interface

（二） Conduct experiment

1、Remove residual gas from the gas path

(1) Open the host, software, and Ar bottle valve (adjust the output pressure to 0.3-0.4 MPa)

(2) Adjust the air circuit: software → measurement → air circuit control → valve 1 → valve 7 (↳) → valve 8 (↱) switch to vent → close the window



(3) Adjust the flow rate: software → measurement → flow setting → 2 # set to 30 ml/min → complete and close the window

Here, channels 1 # and 2 # refer to the instrument carrier gas channel (1 # is the reference port flow rate; 2 # is the test port channel)

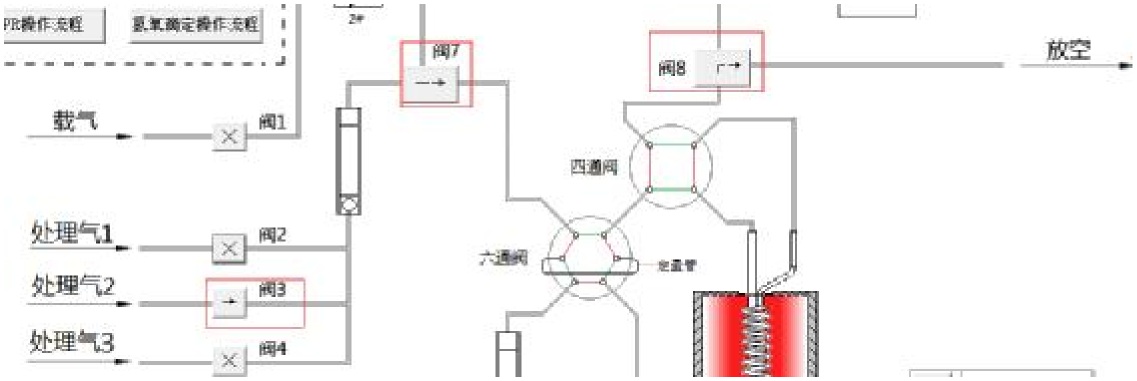
Note: When setting the flow rate, attention should be paid to selecting the corresponding gas to complete the coefficient conversion of the flowmeter. For example, when using a mixed gas, select a gas with a large proportion of components for coefficient conversion.

(4) Purge the sample in an inert gas environment at room temperature for at least 10 minutes

2、Programmed heating and H_2 reduction

(1) Lift the furnace to the designated position, insert the thermocouple into the bottom of the reactor branch pipe, open the H_2 bottle valve, open and adjust the "processing rotameter" to 40ml/min

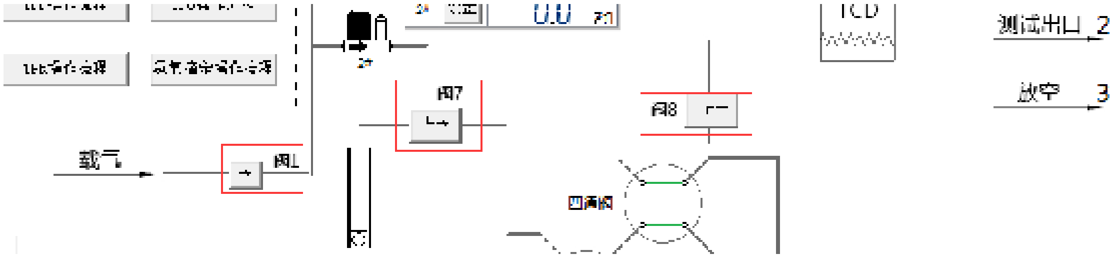
(2) Adjust the air circuit: close valve 1, open valve 3 → valve 7 (→) → valve 8 (┌→) switch to vent → close the window



(3) Set program heating conditions: Measurement → Program heating → Set temperature upper limit, heating rate, and constant temperature time → Add temperature control section → Click to start the program → Close the interface

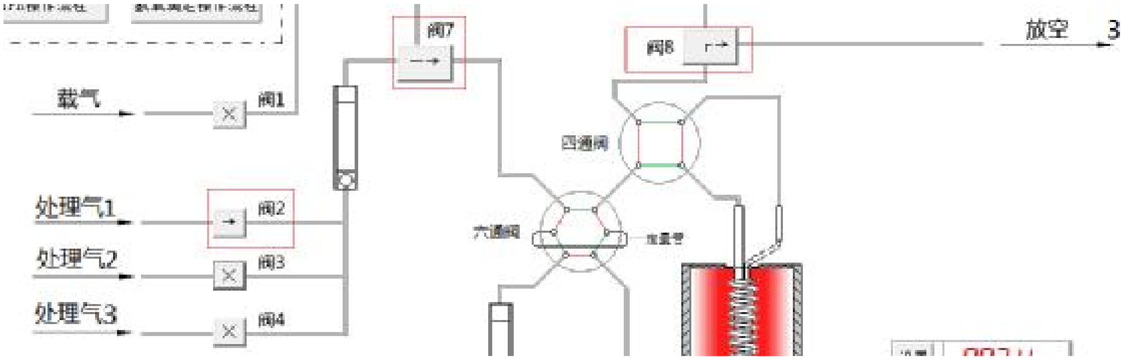
(4) After the program heating program is completed, when the furnace temperature drops below 200 ℃, lower the furnace (to avoid thermocouple damage), continue to use Ar gas for blowing, and proceed with the next operation after the temperature of the sample position returns to room temperature (generally, the strong cooling system requires 30-40 minutes for the furnace body to cool to below 50 ℃)

(5) Remove H2 from the gas path: Close valve 3, open valve 1 → valve 7 (└→) → valve 8 (┌→), switch to venting, and purge with Ar gas for at least 10 minutes



3、Saturated adsorption of O2 at a certain temperature

(1) Adjust the air circuit: close valve 1, open valve 2 → valve 7 (→) → valve 8 (┌→) switch to vent → close the window



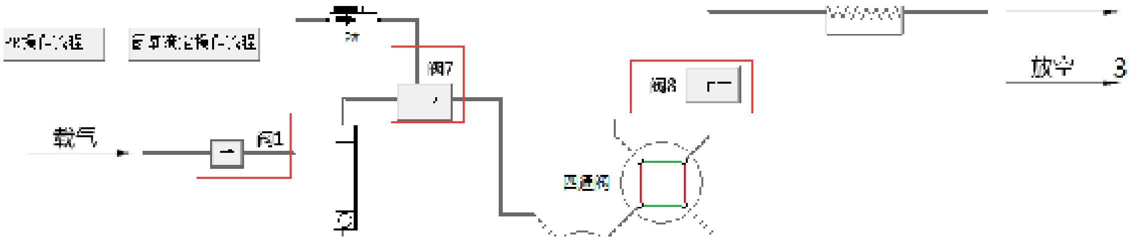
2) Set the O2 adsorption temperature:

① Set temperature: Measure → Program heating → Set upper temperature limit, heating rate, and constant temperature time → Add temperature control section → Click to start the program → Close the interface

② When the set temperature is reached, open the O2 bottle valve and allow pure O2 to adsorb for about 15 minutes

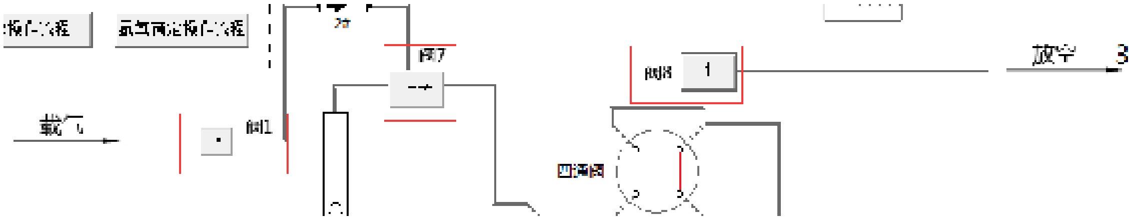
(3) After the program heating program is completed, when the furnace temperature drops below 200 ℃, lower the furnace and continue to use Ar gas for blowing. After the temperature of the sample position returns to room temperature, the next step can be taken

(4) Remove O2 from the gas path: Close valve 3, open valve 1 → valve 7 (└→) → valve 8 (┌→), switch to venting, and purge with Ar gas for at least 10 minutes



4、Pulse H2 titration at a certain temperature

(1) Adjust the air circuit: switch from valve 1 → valve 7 (↳) → valve 8 (↑) to TCD



(2) Adjust the flow rate: Measure → Set the flow rate → Set # 1 to 30ml/min → Set # 2 to 30ml/min → Complete and close the window

(3) Raise the furnace to the designated position

(4) Set H2 titration temperature: Measure → Program heating → Set upper temperature limit, heating rate, and constant temperature time → Add temperature control section → Click to start the program → Close the interface

(5) After the H2 titration temperature is reached, adjust the polarity of TCD to start TCD, and stabilize the baseline leveling (multiple zeroing is required during the stabilization process, and the voltage variation range is ± 20 μ V)

(6) Adjust the gas path: maintain the current gas path, open valve 5, adjust the " pulse rotor flowmeter" to 40ml/min, and stabilize for 10 minutes

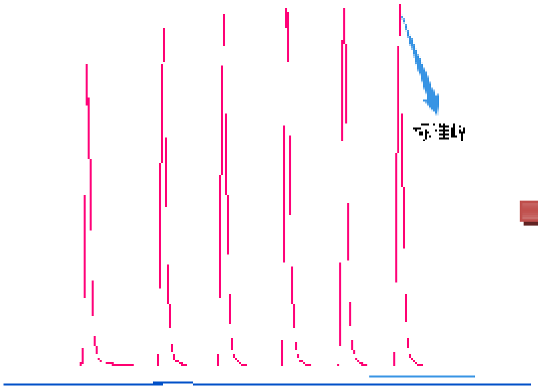
(7) Pulse test: inject the first H2 pulse in cooperation with the six way valve, adjust the zero point after the baseline is leveled, inject the second H2 pulse... until the last pulse peak and the peak area of the previous pulse peak are the same and stop at the same time

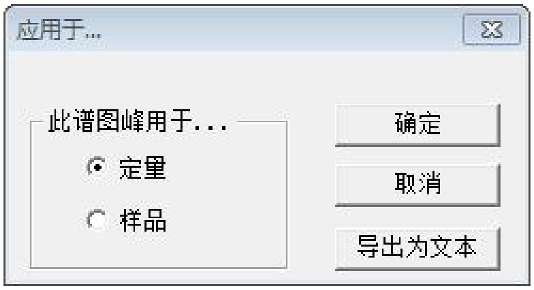
(三) Experimental completion

Save experimental data, close TCD thermal conductivity cell, close cylinder valve, close chemical adsorption instrument host, and recycle or dispose of samples

(四) Data processing

Software → Click on the "Peak Identification" button (select the standard peak on the software interface) → Quantitative → Confirm → Enter the volume of the quantitative ring (see the label on the back of the instrument host) → Close → Click on the "Peak Identification" button (select the remaining adsorption peak on the software interface) → Sample → Confirm → Click on the report window → Select the hydrogen oxygen titration report → Enter experimental parameters

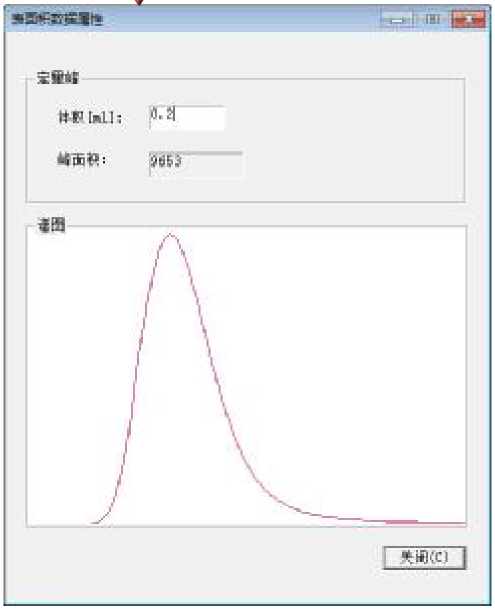



应用于...

此谱图峰用于...

● 定量

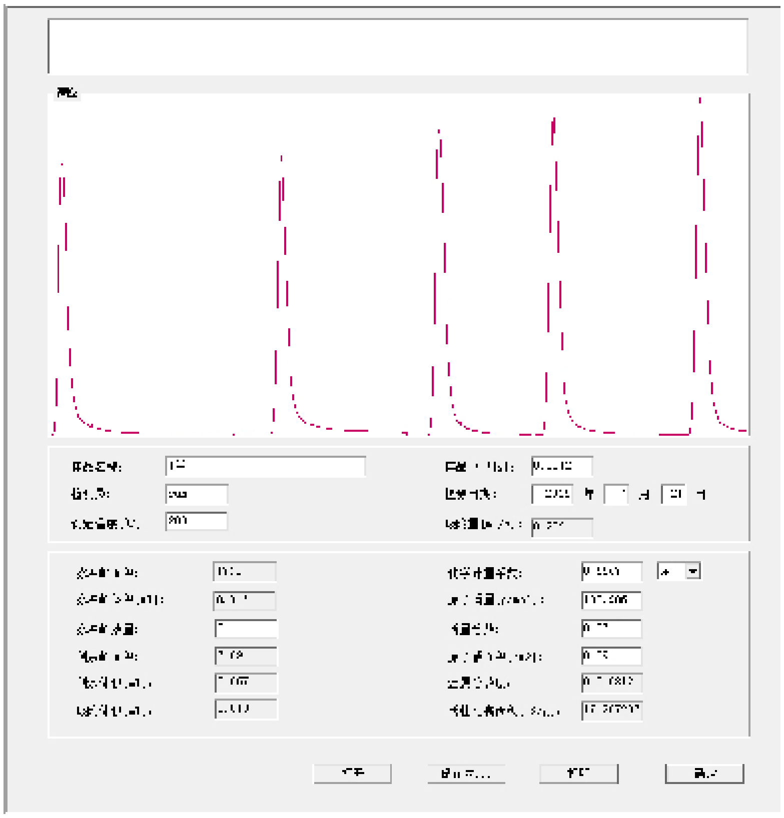
○ 样品


定量峰

体积[mL]: 0.2

峰面积: 9653

谱图



（五） Data analysis

This equipment analysis software provides a data analysis module for characterizing catalyst indicators such as metal dispersion, active surface area, and average grain size. For specific experimental data acquisition and calculation applications, please refer to the following instructions:

1. Metal dispersion:

1) Definition: Metal dispersion refers to the ratio of the number of active metal atoms on the catalyst surface to the total number of metal atoms in the catalyst.

2) Application formula:

$$D = \frac{n \times V_g \times M_M}{W \times P \times 22414} \qquad (1)$$

In the formula：

D ： Catalyst metal dispersion；

n ：The stoichiometric coefficient of the analyzed gas during the actual reaction process For the stoichiometric formula of hydrogen oxygen titration, different literature has provided different results. For example, when hydrogen titration is used to determine the chemical adsorption of oxygen on Pt, one oxygen atom on Pt consumes two hydrogen atoms and reacts to form water, which is adsorbed on the carrier. At the same time, due to the fact that Pt atoms themselves need to adsorb one hydrogen atom after deoxidation, the amount of hydrogen used to titrate the oxygen atoms adsorbed on Pt itself is only 2/3 of the total hydrogen consumption, that is, surface Pt If the atomic number is 2/3 of the consumed H2 molecule, then the stoichiometric coefficient is taken as 2/3. In fact, the exact stoichiometric formula and coefficient to be used must be determined by supplementary experiments

M_M：Relative atomic mass of catalyst metal,Unit (g/mol)

W ：Mass of the tested sample, in grams

P ：Mass fraction of active metals in catalysts，%

3）Calculation of Vg：

$$V_g = \frac{NA_i - A_{II}}{A_i} \times V \qquad (2)$$

In the formula：

Vg：Represents the volume of analytical gas (H2 or O2) consumed by the catalyst sample that has been completely oxidized (or reduced) during the experimental process, in milliliters (milliliters)；

Ai：The chromatographic peak area caused by injecting an analytical gas pulse during no-load (without sample) (please refer to the software instructions for peak cutting operation);

AⅡ：The chromatographic peak area caused by the overflow of the analytical instrument from the beginning of pulse titration to the saturation of titration (please refer to the software instructions for peak cutting operation);

V：Instrument pulse quantitative tube volume, in milliliters, with built-in parameters of the instrument;

N：The number of pulses injected from the beginning of pulse titration to the saturation of titration。

2、 Active metal specific surface area：

1）Definition: The surface area of surface active metal atoms in a unit mass catalyst.

2）Application formula：

$$S = \frac{2 \times V_g \times N_0 \times \sigma_M}{W \times P \times 22414} \times 10^{-18} \qquad (3)$$

In the formula：

S ：Catalyst activity specific surface area， Unit (square meter/gram) m^2/g

V_g ：Represents the volume of analytical gas (H2 or O2) consumed by the catalyst sample that has been completely oxidized (or reduced) during the experimental process, in milliliters (milliliters)；

N_0 ：Avogadro constant，6.02×10^{23} /mol

σ_M ：Cross sectional area of catalyst metal atoms，$0.089 nm^2$（Square nanometer）

W ：Mass of the tested sample，Unit g (grams)

P ：Mass fraction of active metals in catalysts，%

3、Average grain size

1) Definition: The average particle size of the catalyst active metal (for Pt, the average grain size is estimated based on the Hughes model). Its basic assumption is that all Pt grains are ideal, a cube of the same size, with one face in contact with the support, and the other five faces exposed. The length d and surface area S of one side of the cube, as well as volume V or density ρ Regarding.)

2） Application formula：

$$d = \frac{5 \times 10^4}{\rho_M \times S} \qquad (4)$$

In the formula：

d：Average grain size of catalyst metal，unit (Angstrom) Ǻ

S ：Catalyst activity specific surface area， Unit (square meter/gram) m^2/g

ρ_M：Catalyst metal density，Unit (g/cm3) g/cm^3

4、Table of Common Catalytic Metal Parameters

No	name of metal	Relative atomic mass of elements（g/mol）	Atomic cross-sectional area （nm2）	Density（g/ml）
1	Pt（铂）	195.08	0.089	21.45
2	Pd（钯）	106.42	Unknown	12.02
3	Re（铼）	186.207	Unknown	21.04
4	Ru（钌）	101.07	Unknown	12.37
5	Ni（镍）	58.69	Unknown	8.9
6	Co（钴）	58.933	Unknown	8.9
7	Fe（铁）	55.84	Unknown	7.874
8	Ag（银）	107.868	Unknown	10.5
9	Cu（铜）	63.54	Unknown	8.96
10	Zn（锌）	65.38	Unknown	7.13

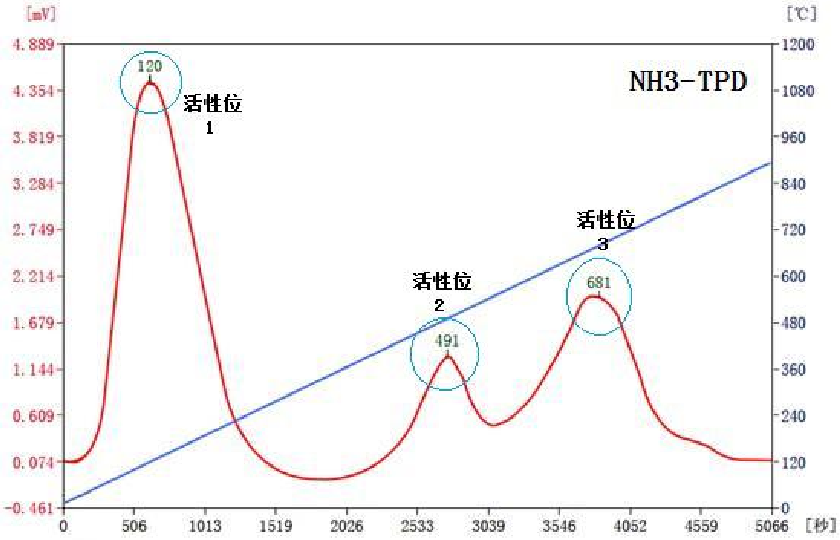
（Basic calculation is for precious metals 1-4）

Chapter 7 Experimental Analysis

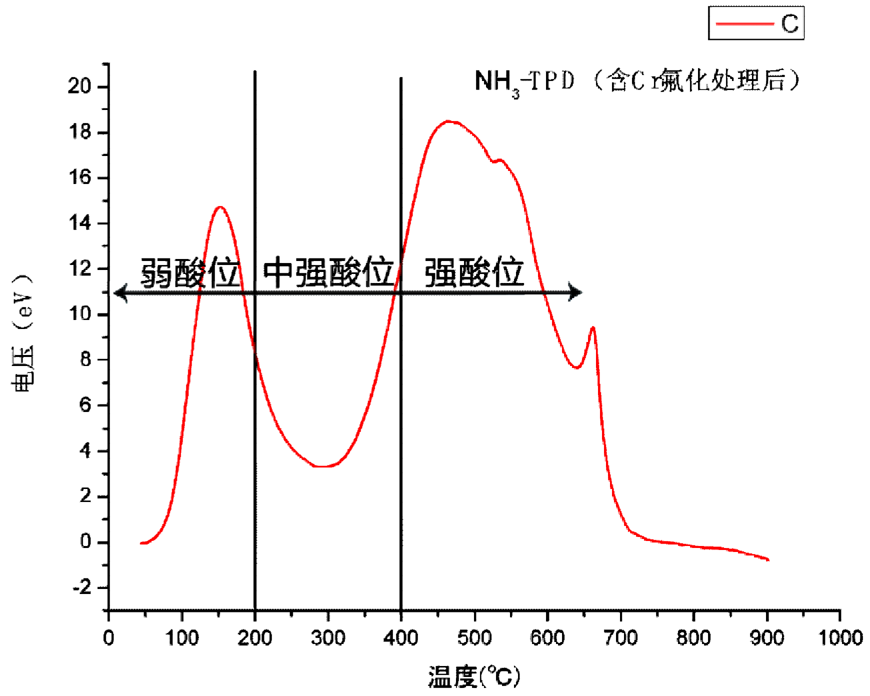
一、 Experimental Analysis of NH3-TPD

TPD（temperature programmed desorption）

NH_3-TPD is an experimental method for characterizing the acidity of catalysts. This experiment uses carrier gas (usually inert gases such as N_2 Ar He) under certain temperature programmed conditions, passes through the catalyst bed, and uses a thermal conductivity (or mass spectrometry) detector to determine the concentration signal of NH_3 desorbed by the catalyst at each temperature point in the carrier gas (different acidic sites, adsorbed substances usually desorb at different temperatures), From the obtained TPD spectrum, information such as desorption peaks and desorption temperature points can be obtained, including the number of acidic sites, acidic center temperature, and acid strength. Acid value can also be obtained through different "quantitative" methods in the experiment。



There is a linear relationship between the adsorption force of NH3 on the sample and the acidity of the adsorption site. The stronger the acidity of the adsorption site, the greater the adsorption force of NH_3, and the higher the temperature required for desorption. Characterization of the acidity distribution of the sample by analyzing the amount of NH3 content in the desorption gas at different temperatures. In the field of catalysis, it is generally believed that desorption peaks below 200 ℃ correspond to weak acid sites, desorption peaks in the temperature range of 200-400 ℃ correspond to medium strong acid sites, and desorption peaks above 400 ℃ correspond to strong acid sites.



How should NH3-TPD experiments be operated and what problems may exist during this process?

1. Selection of gas usage

Process gas: choose high-purity NH_3

PS：Why not use a mixture of low concentration inert gas and NH_3?

At 20 ℃, the liquefaction pressure of NH3 is about 0.86Mpa, and the pressure of the mixed gas cylinder is generally around 10Mpa. At this time, NH3 in the steel cylinder accumulates at the bottom of the cylinder in a liquefied state, and the actual output concentration of NH3 is much lower than the percentage of the ratio; Due to the low concentration of the output, during a certain period of adsorption, it may occur that the adsorption saturation state has not been reached, resulting in significant deviation in the test results.

Carrier gas: Choose high-purity Ar, high-purity N2, or high-purity He.

2. Experimental conditions

The experimental conditions mainly include the following points:

(1) Sample processing and loading amount: For chemical adsorption testing, in order to ensure the passability of the test gas, the sample needs to be compressed and sieved through a 40-60 mesh sieve (if conditions are not met, ensure that the particle size is consistent for each test); Comparative experiments need to ensure consistency in the sample size, which is generally 50mg-100mg. For samples with unsatisfactory testing results or low content of the tested substance, the sample size can be appropriately increased.

(2) Dehydration temperature: Select an appropriate processing temperature based on the type of sample to avoid changes in composition or structure of the sample caused by high temperature; The most common treatment temperature is between 200 and 300 ℃. For some samples with well-developed pores, a higher treatment temperature (300 to 500 ℃) may be chosen. For high-temperature treatment, attention should be paid to avoiding the precipitation and decomposition of the load.

(3) The adsorption temperature and physical adsorption removal of NH3: Based on the sample situation, the adsorption temperature is selected between 50-100 ℃. Currently, the most commonly used adsorption temperature condition is 100 ℃, and the adsorption process adopts two methods: pulse quantitative adsorption or saturated adsorption.

PS：How to determine if the adsorption is saturated?

① *Pulse adsorption until there is no change in the peak area of the pulse to determine adsorption saturation. Some researchers also use the number and area of adsorption peaks to determine the "amount" of chemically adsorbed or desorbed ammonia, but this method is not rigorous. Firstly, there will be significant physical adsorption during the adsorption process. Secondly, the peak emergence process is a concentration change curve under the influence of heating rate, which has poor consistency with the pulse peak area.*

② *The sample undergoes saturated adsorption under a certain flow rate of high-purity NH3 gas flow, usually requiring at least 20 minutes to ensure sufficient adsorption of ammonia by the sample. The adsorption of NH_3 at a certain temperature is relatively easy, but the concentration and adsorption time need to be guaranteed.*

(4) Programmed temperature rise: The conditions for programmed temperature rise are quite critical, and different conditions will result in different experimental results. For example, differences in peak temperature, whether signal peaks at different acidic sites are "separated", etc. So what are the conditions included?

① Heating rate: The commonly used heating rate is 10 ℃/min. Many experiments show that the "peak separation" is not obvious or even "becomes" a sample peak, and the rapid heating rate is one of the factors that cause this problem. In addition, an excessively fast heating rate can also cause a lag in the peak temperature.

② Carrier gas flow rate: The commonly used carrier gas flow rate is 30ml/min; The carrier gas flow rate, as a reaction condition, directly affects the peak temperature. Generally, a decrease in flow rate will increase the peak temperature.

③ Upper temperature limit: Generally, the test temperature for this experiment is within 700 ℃, and excessively high temperatures are often meaningless.

3. Common experimental problems

(1) Calculation of acid content: The experimental process of "acid content" in NH3-TPD testing is relatively complex, mainly including the following methods

① Standard pulse peak calibration method: Compare the sample signal peak area with the standard pulse peak area, calculate the NH3 volume of the sample peak area, and then calculate the "acid amount". But the peak process is a concentration change curve under the influence of heating rate, which has poor consistency with the pulse peak area.

② Tail gas absorption titration method: This method is currently recognized as a relatively reliable method, which uses diluted acid solution for tail gas absorption, determines the amount of NH3 desorbed through reverse titration, and then calculates the "acid amount". It is worth noting that after the adsorption is completed, the exhaust pipe should be removed from the absorption tank in a timely manner to avoid acid solution backsuction after gas interruption. Backsuction will have a certain impact on the detector and other components of the instrument, and even damage.

③ Solid acid calibration method: This method is theoretically feasible and has not yet been reported. The experimental process is the same as the calibration method of TPR, using standard materials to obtain the NH3 amount corresponding to the peak area, and then comparing it with the test peak area to calculate the amount of NH3 removed

(2) What data processing problems will be encountered during the experiment?

① How to determine the acid content of an acidic site when multiple acidic sites exist simultaneously and the test peaks are not completely separated?

PS: Peak division can be simulated using Origin software to obtain the corresponding peak area before calculation.

② How to choose the conditions such as peak area calibration and sample size for standard samples?

PS: It is necessary to ensure that the sample size and testing conditions are consistent with the tested sample.

③ How is the amount of NH3 determined when calibrating the peak area of pulse peak and solid acid?

PS: The amount of NH3 in the pulse peak is obtained through the volume of the "quantitative ring", which varies from 50 μ L to 200 μ L. Generally, each instrument is equipped with a fixed volume quantitative ring before leaving the factory; The peak area consumption of NH3 for calibration of standard samples is calculated based on the theoretical consumption of NH3 for standard samples.

(3) What is the "tail dragging" of the peak?

The main reason for this is the rise in gas temperature, which causes the TCD signal to produce a "temperature drift". Generally, the influence of gas temperature on TCD signals does not show significant signal differences, and the decomposed and extracted substances of the sample often have sustained and strong effects.

(4) What are the "negative peaks" in the test results?

The "negative peak" refers to the peak shape that is opposite to the result of the tested substance in the experiment; This phenomenon is relatively rare in TPD experiments, and the opposite peak shape is mainly caused by the following situations, which need to be determined based on the actual experimental situation.

① The removal of H_2O from the sample, such as the incomplete removal of H_2O adsorbed by the sample.

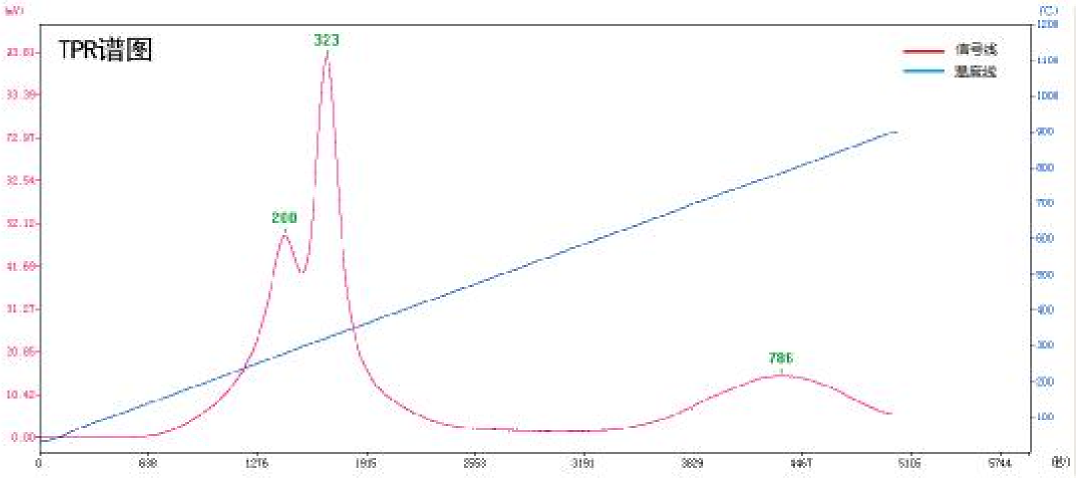
② NH_3 undergoes decomposition under high-temperature catalysis..

③ Decomposition of sample load or carrier under high temperature.

二、Analysis of TPR Experiment

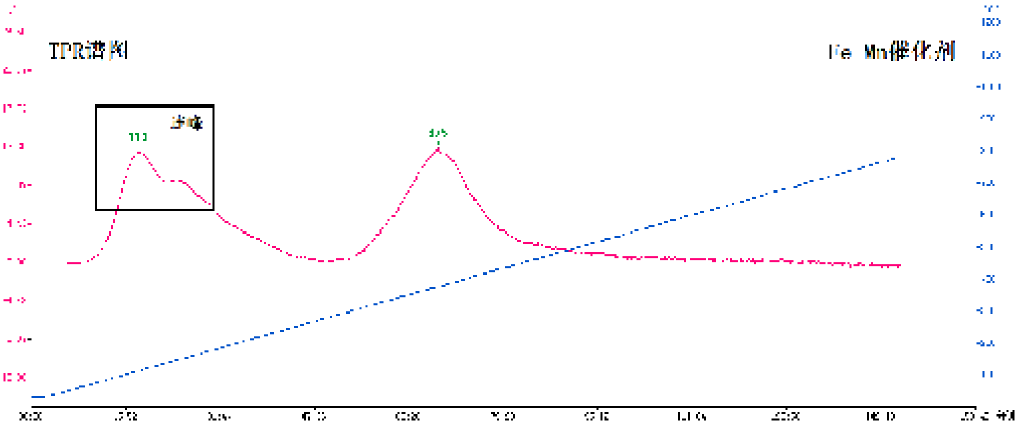
Analysis of TPR (Temperature Programmed Reduction) Experiment

This experiment uses reduced gas (Ar/H_2 or N_2/H_2) under certain programmed heating conditions, passes through the catalyst bed, and measures the hydrogen concentration signal at each temperature point using a thermal conductivity (or mass spectrometry) detector to obtain the reduction performance of the catalyst。



The temperature at which metal oxides and metal salts are reduced depends on their chemical properties. If other substances are doped into a single substance and there are interactions between the substances that change the properties of the original substance, the reduction temperature will also change accordingly. Based on the degree to which the reduction temperature of the mixture deviates from the reduction temperature of the pure compound (this deviation mainly refers to the changes in the peak temperature and peak temperature range), we can infer the interaction between the components.

In TPR experiments, "standard samples" can be used to "calibrate" the peak area. After calibration, we can obtain the amount of "hydrogen" consumed based on the peak area of the sample testing, and then calculate the amount of reduced substance; In addition to obtaining the amount of reducing substance, we can also obtain the valence state of the reduced substance. When different valence states coexist in the same substance, they often appear as two inseparable "continuous peaks" in the spectrum。



How should TPR experiments be operated and what problems may exist during this process?

1. Selection of gas usage

Process gas: Select high-purity Ar and high-purity He

Carrier gas (reaction gas): Select a high-purity Ar/ H_2 (H_2 is 5% -10%) mixture

Note: N_2 and N_2/H_2 mixtures should be avoided as much as possible, as some samples may react or adsorb with N_2, such as Ag_3N.

2. Experimental conditions

The experimental conditions mainly include the following points:

(1) Sample processing and loading amount: For chemical adsorption testing, in order to ensure the passing of the test gas, the sample needs to be compressed and sieved through 40-60 mesh screens (if conditions are not met, ensure that the particle size is consistent for each test); Comparative experiments need to ensure consistency in the sample size, which is generally 50mg-100mg. For samples with unsatisfactory testing results or low content of the tested substance, the sample size can be appropriately increased.

(2) Dehydration temperature: Select an appropriate treatment temperature based on the type of sample to avoid changes in composition or structure of the sample caused by high temperature; The most common treatment temperature is between 200 and 300 ℃. For some samples with well-developed pores, a higher treatment temperature (300 to 500 ℃) may be chosen. For high-temperature treatment, attention should be paid to avoiding the precipitation and decomposition of the load.

(3) Programmed temperature rise: The conditions for programmed temperature rise are quite critical, and different conditions will result in different experimental results. For example, the difference in peak temperature and whether the reduction peaks of the two substances are "separated". So what are the conditions included?

① Heating rate: The commonly used heating rate is 10 ℃/min. Many experiments show that the "peak separation" is not obvious or even "becomes" a sample peak, and the rapid heating rate is one of the factors that cause this problem.

② Carrier gas flow rate: The commonly used carrier gas flow rate is 30ml/min; The carrier gas flow rate, as a reaction condition, directly affects the peak temperature. Generally, a decrease in flow rate will increase the peak temperature.

3. Common experimental problems

(1) How to determine the hydrogen consumption of the experiment?

① Standard pulse peak for peak area calibration

② Peak area calibration using standard copper oxide

When multiple substances or a single substance has multiple valence states, the test peaks are not completely separated. To determine the hydrogen consumption of each component, the origin software needs to simulate the peak separation, obtain the corresponding peak area, and then calculate.

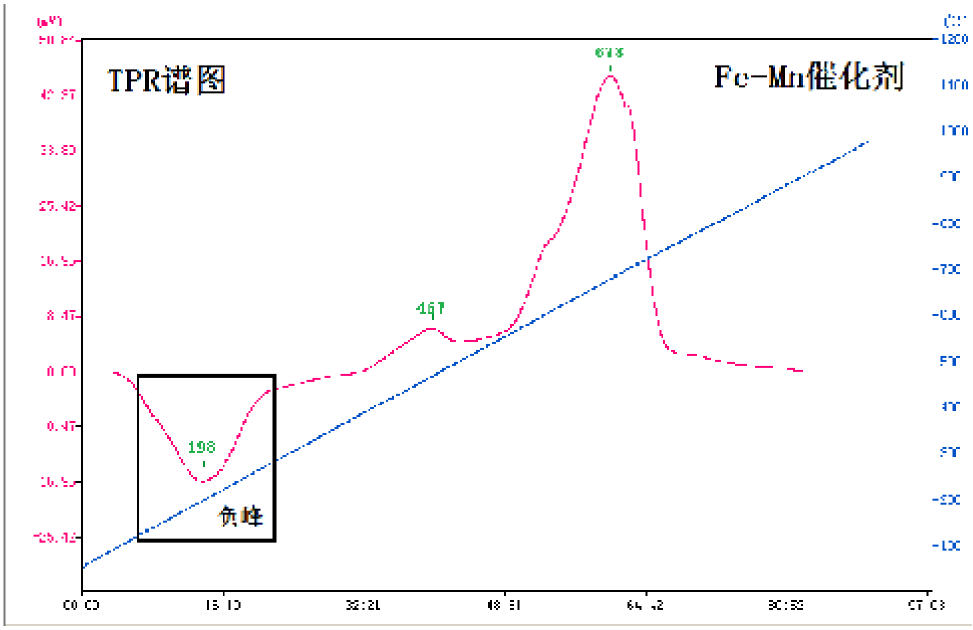
How to choose the conditions such as peak area calibration and sample size for standard samples?

It is necessary to ensure that the sample size and testing conditions are consistent with the tested sample.

How is the amount of H2 determined when calibrating the peak area of the pulse peak?

The amount of H2 in the pulse peak is obtained through the volume of the "quantitative ring", which varies from 50 μ L to 200 μ L. Generally, each instrument is equipped with a fixed volume quantitative ring before leaving the factory; The peak area hydrogen consumption calibrated by the standard sample is obtained by calculating the theoretical hydrogen consumption of the standard sample.

(2) What is the "negative peak" in the test results?



The "negative peak" refers to the peak shape that is opposite to the result of the tested substance in the experiment; The opposite front shape in TPR experiment is mainly caused by the following situations, and the specific situation needs to be determined based on the actual experimental situation.

① H_2O generated by reaction

② HCl generated by reaction

③ CH4 generated by reaction

④ Material undergoes "dehydrogenation" phenomenon (hydrogen overflow)

⑤ H_2O adsorbed by the material itself

How to judge and solve the above situation?

① Negative peak generated by H_2O

If there is a negative peak in the low-temperature range, it is likely to be an adsorbed water peak; The water peak can be divided into two situations: adsorption of H_2O and reaction of H_2O. We can replace the carrier gas with Ar and conduct experiments on samples treated under the same conditions. If the negative peak still exists, it indicates that it is adsorption of H_2O. If it disappears, it indicates reaction of H_2O; The negative peak appearing in the reaction of H_2O often occurs when the content of the loaded substance is too low (usually manifested as weakening the peak signal); The H_2O peak signal can be removed by setting a cold trap before TCD.

② Negative peak generated by hydrogen overflow

After excluding the influence of H_2O peaks through a cold trap, some negative peaks may also appear, which may be hydrogen overflow; Hydrogen overflow is the phenomenon of hydrogen chemical bond decomposition in the catalyst, resulting in dehydrogenation, which increases the concentration of hydrogen in the mixed gas. This phenomenon occurs at the application temperature of the catalyst and is considered beneficial for catalytic reactions. The concentration of H_2 in TPR decreased, and the test results showed a positive peak; On the contrary, it will exhibit negative peaks. Hydrogen overflow occurs in numerous catalytic reactions. In addition, hydrogen and precious metals such as Pt generate hydrides that also decompose at high temperatures, and such negative peaks often occur at higher temperatures; There is also a dehydrogenation phenomenon, which is common when the specific surface area of the sample is large. At low temperatures, the sample adsorbs hydrogen gas, and at high temperatures, it desorbs, leading to negative peaks. This situation is relatively rare because the desorption temperature of hydrogen gas is relatively low.

③ Negative peak generated by the compound generated by the reaction

There is carbon deposition in the sample preparation or used catalysts, and methane will be generated during the TPR process. On the one hand, the existence of carbon deposition is demonstrated, and the temperature at which methane occurs is also demonstrated; There are also some metal salts that produce products during TPR experiments, such as HCl produced after CuCl reduction; The above products can be removed by filling the cold trap tube with adsorbent to remove the negative peak and its impact on the experimental results.

(3) After the experiment is completed, there is material sintering on the reactor tube wall

This phenomenon is due to the high reduction temperature causing the precipitation of loaded metal elements, which are sintered on the pipe wall; Therefore, when conducting TPR experiments, it is necessary to pay attention to the experimental temperature, as excessively high temperatures may not necessarily be meaningful.

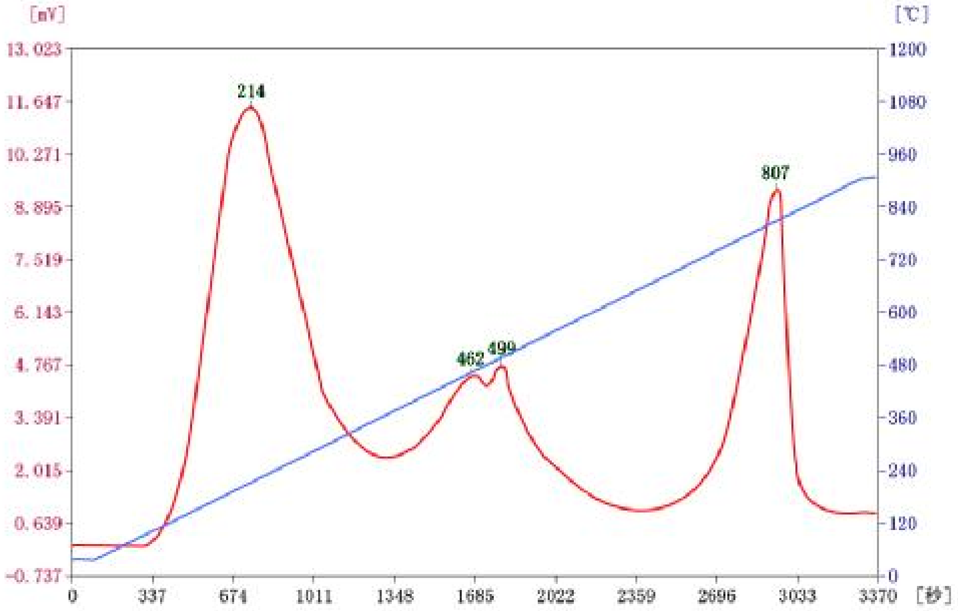
(4) TCD signal cannot return to "zero point"

This problem is mainly caused by two factors. One is that the high temperature increases the gas temperature, causing a difference between the gas temperature at the TCD test port and the reference port, resulting in a signal value of "temperature drift"; Another reason is that the test sample continues to experience gas consumption or reactant generation.

三、 Experimental Analysis of O_2 TPD

Temperature programmed desorption of O_2 TPD, i.e. oxygen（oxygen temperature programming desorption）

The O_2-TPD experiment is currently the main method used to study the oxygen storage performance of catalysts (crystal nucleus oxygen and adsorbed oxygen). This experiment uses a thermal conductivity detector under certain programmed heating conditions to measure the oxygen concentration signals desorbed by the catalyst at various temperature points, and obtain the oxygen storage capacity and active sites of the catalyst. In addition, the oxygen storage capacity in ternary catalysis is measured using the method of oxygen pulse titration.



O$_2$-TPD 实验

How should the O$_2$-TPD experiment be operated and what problems may exist during this process?

1. Selection of gas usage

Process gas: Select high-purity oxygen gas O$_2$

Carrier gas: Select high-purity helium He

2. Experimental conditions

The experimental conditions mainly include the following points:

(1) Sample processing and loading amount: For chemical adsorption testing, in order to ensure the passing of the test gas, the sample needs to be compressed and sieved through 40-60 mesh screens (if conditions are not met, ensure that the particle size is consistent for each test); Comparative experiments need to ensure consistency in the sample size, which is generally 50mg-100mg. For samples with unsatisfactory testing results or low content of the tested substance, the sample size can be appropriately increased.

(2) Dehydration temperature: In oxygen desorption testing, crystal nucleus oxygen is the key point, so the dehydration temperature should not be too high to avoid the precipitation of crystal nucleus oxygen caused by excessive temperature.

Therefore, it is recommended to set the dehydration temperature within 200 ℃. If the sample cannot be completely removed at 200 ℃ due to the presence of crystalline water, a low-temperature cold well can be used for condensation removal in the experiment to avoid water signals affecting the test signal results.

(3) Oxygen adsorption: In order to test the oxygen adsorption capacity (amount of desorbed oxygen) of the sample during testing, it is necessary to perform oxygen adsorption on the catalyst. Therefore, the adsorption temperature is crucial, as oxygen has a certain oxidation capacity. Excessive temperature can change the valence state of the catalyst load, and at the same time, excessive temperature can also cause the precipitation of crystal nucleus oxygen. It is recommended to set the oxygen adsorption temperature below 200 ℃, with the most common conditions being 100 ℃ and 200 ℃.

(4) Programmed temperature rise: The programmed temperature rise conditions are quite critical, and different experimental results may occur depending on the conditions. The general testing conditions for the PCA-1200 chemical adsorption instrument are: carrier gas flow rate 30ml/min, and heating rate 10 ℃/min. A decrease in heating rate will cause a decrease in peak temperature, while a decrease in carrier gas flow rate will cause an increase in peak temperature.

3. Common experimental problems

(1) How to determine the source of oxygen, whether it is crystal nucleus oxygen or adsorbed oxygen?

① The catalyst can be labeled using isotope tracing method

It is a microanalysis method that uses radioactive nuclides as tracers to label research objects. Tracer atoms, also known as labeled atoms, are atoms with easily detectable nuclear physical characteristics.

② X-ray photoelectron spectroscopy, also known as XPS

It is a spectroscopic method that uses high-energy photons with wavelengths in the X-ray range to irradiate the measured sample and measure the resulting photoelectron energy distribution.

③ Determine by desorption temperature

The desorption of crystal nucleus oxygen generally requires a certain amount of energy, so the temperature of the desorption peak is often above 300 ℃, while the adsorbed oxygen is often within 200 ℃.

四、Experimental Analysis of Active Metal Dispersion

Active Metal dispersion refers to the ratio of the number of metal atoms distributed on the surface of the carrier to the total number of atoms on the carrier. For metal dispersion testing, the active components tested mainly include Pt, Pd, Rh, Ni, Cu, etc. At present, the most commonly used testing methods for metal dispersion are chemical adsorption method, namely pulse titration method and static volumetric method.

1. Testing Method and Principle of Metal Dispersion

(1) The principle of chemical adsorption method for measuring metal dispersion

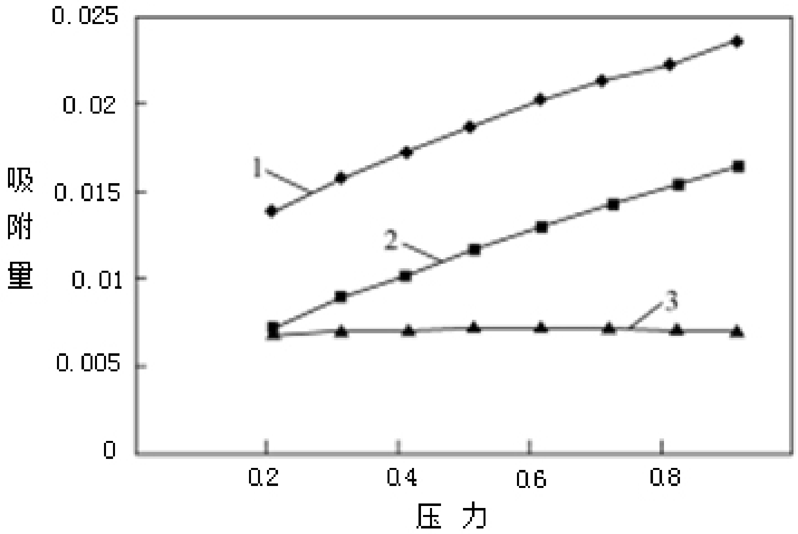
The chemical adsorption method utilizes certain probe molecules (such as H2, O2, CO, etc.) to adsorb onto a metal surface in a chemically constructed form. By measuring the chemical adsorption capacity of the probe molecules, the dispersion and active surface area of the metal can be calculated. During the testing process, the pulse titration method requires that the probe molecules do not have any adsorption with the carrier, while the static volumetric method only requires that the probe molecules do not have chemical adsorption with the carrier. Similarly, the chemical adsorption form of the probe molecules with the tested metal conforms to a certain stoichiometric coefficient.

(2) The main method for measuring the dispersion of metals by chemical adsorption method

① Static capacity method

The static capacity method uses a physical adsorption instrument (specific surface area and pore size analyzer) to conduct two consecutive isothermal adsorption tests for H2 on the tested sample, obtaining two isothermal adsorption lines for H2. Due to the irreversibility of chemical adsorption, the fitting curve of chemical adsorption capacity can be obtained by comparing the adsorption capacity of two curves at different partial pressures, and then the H2 chemical adsorption capacity can be obtained. Data such as metal dispersion and active surface area can be calculated.

As shown in the figure:



Isothermal adsorption test of H2 (static capacity method)

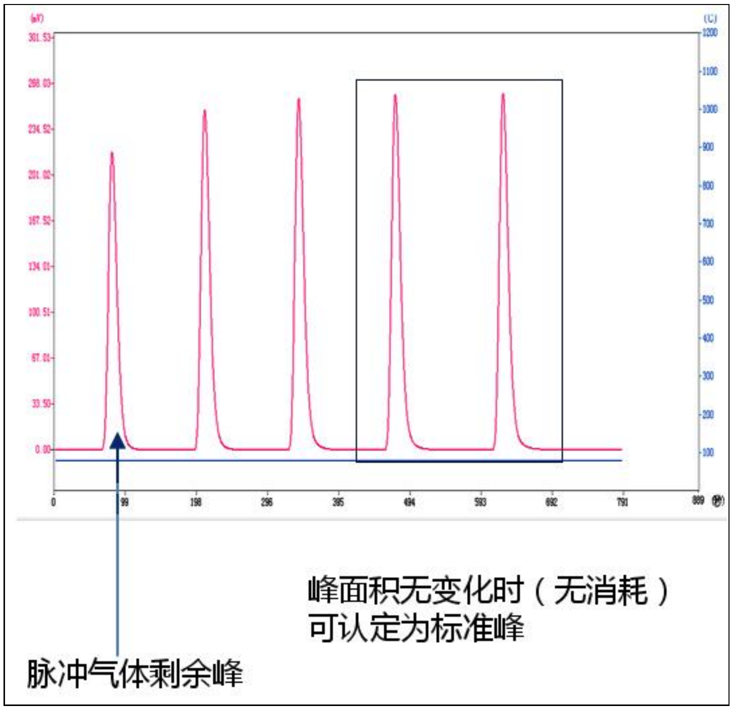
There are two isotherm adsorption curves for H2 in the figure:

- The No.1 isothermal adsorption curve represents the reversible, irreversible, and physical adsorption isotherms of H2 on the metal surface.
- The No. 2 isothermal adsorption curve shows the irreversible chemical adsorption and physical adsorption of H2 on the metal surface.
- The third curve is a fitting curve for the chemical adsorption capacity, and its intercept from the vertical axis is the chemical adsorption capacity of the probe gas on the surface metal.

So how was curve 3 obtained? Why is this curve the chemical adsorption capacity of the probe gas? Due to the irreversibility of chemical adsorption, after the completion of curve 1 testing, the reversible chemical adsorption and physical adsorption of H2 can be removed through vacuum treatment, retaining the irreversible chemical adsorption of H2 on the metal surface. Under the same experimental conditions, the No. 2 isothermal adsorption curve was measured. Due to the occupation of irreversible chemical adsorption sites, only reversible chemical adsorption and physical adsorption can occur this time, resulting in a difference in the amount of H2 adsorption. The difference between the two adsorption isotherms is irreversible chemical adsorption.

② Pulse titration method (dynamic chemical adsorption method)

Pulse titration method is an experiment using a dynamic chemical adsorption instrument to perform O2 titration and H2 titration on a catalyst that has been reduced by H2. Finally, data such as metal dispersion and active surface area are obtained by calculating the consumption of H2.



Pulse titration method (dynamic chemical adsorption method)

It should be noted that during the experiment, the signal displayed in the spectrum is the residual quantity, not the consumption quantity. When the sample no longer consumes pulse gas, the peak area will not change, and we consider the unchanged peak area as the standard peak (corresponding to a certain volume of pulse gas). We can obtain the consumption volume of H2 by comparing the area difference between the remaining peak and the standard peak.

③ Calculation formula

a) Metal dispersion: Metal dispersion refers to the ratio of the number of active metal atoms on the catalyst surface to the total number of metal atoms in the catalyst

Application formula：$D = \frac{n \times V_g \times M_M}{W \times P \times 22414}$

Explanation: The stoichiometric coefficient of the analyzed gas during the actual reaction process For the stoichiometric formula of hydrogen and oxygen titration, different literature has provided different results. For example, when hydrogen titration is used to determine the chemical adsorption of oxygen on Pt, one oxygen atom on Pt consumes two hydrogen atoms to react and generate water, which is adsorbed on the carrier. At the same time, due to the fact that Pt atoms naturally adsorb one hydrogen atom after deoxygenation, the amount of hydrogen used to titrate the oxygen atoms adsorbed on Pt itself is only 2/3 of the total hydrogen consumption, which is the surface Pt If the sub number is 2/3 of the consumed H2 molecules, then the stoichiometric coefficient is taken as 2/3. In fact, the exact stoichiometric formula and coefficient to be used must be determined by supplementary experiments.

Vg：Indicates the volume of analytical gas consumed by the catalyst sample that has been completely oxidized (or reduced) during the experimental process，Unit(ml)；

n ：Stoichiometric coefficient

M_M： Relative atomic mass of catalyst metal,Unit (g/mol)

W ：Mass of the tested sample，Unit g (grams)

P ：Mass fraction of active metals in catalysts，%

b) Active specific surface area: The surface area of surface active metal atoms per unit mass of catalyst。

Application formula：$S = \frac{2 \times V_g \times N_0 \times \sigma_M}{W \times P \times 22414} \times 10^{-18}$

S ：Catalyst activity specific surface area， Unit (square meter/gram) m^2/g

V_g ：Represents the volume of analytical gas (H2 or O2) consumed by the catalyst sample that has been completely oxidized (or reduced) during the experimental process, in milliliters (milliliters)；

N_0 ：Avogadro constant，6.02×10^{23} /mol

σ_M ：Cross sectional area of catalyst metal atoms，0.089nm^2（Square nanometer）

W ：Mass of the tested sample，Unit g (grams)

P ：Mass fraction of active metals in catalysts，%

2. Experimental Conditions and Problems of Dynamic Chemical Adsorption (Taking PCA-1200 as an Example)

(1) Selection of gas usage

Pulse gas: high-purity O_2, high-purity H_2; Select high-purity CO when testing metal Ni

Carrier gas: Select high-purity N_2 and high-purity Ar; Select high-purity He when testing metal Ni

Process gas and reaction gas should be selected with a purity of 99.999% or higher as much as possible.

(2) Experimental conditions

The experimental conditions mainly include the following points:

① Sample processing and loading volume

For metal dispersion testing, to ensure consistency in testing, the sample needs to ensure consistency in particle size during each test; The general sample size is 50mg-100mg. For samples with unsatisfactory testing results or low content of the tested substance, the sample size can be appropriately increased, but it should not be too much to avoid hydrogen overflow, which may lead to larger testing errors and poor repeatability.

② Dehydration temperature

For the vast majority of catalysts, the dehydration temperature depends on the material's tolerance temperature and the form of water present in the tested sample. When the sample can withstand higher temperatures, it is recommended to have a dehydration temperature of 300-400 ℃;

③ Reduction temperature

It is necessary to choose an appropriate reduction temperature based on the sample situation to ensure that the tested component is in a elemental state before the "pulse titration" experiment. Many Pt/Rh/Pd catalysts often require a higher reduction temperature, typically between 300 and 500 ℃.

④ Oxidation temperature and titration temperature

For the vast majority of samples, 100 ℃ is relatively reasonable; Of course, if the activity of the catalyst is strong enough, there is no problem at room temperature. For supported catalysts such as Ni/Cuo, this temperature may need to be appropriately increased (the metal dispersion test of Ni based catalysts cannot oxidize).

(3) Common experimental problems

① What is the significance of using cold traps in pulse experiments

The function of a cold trap is to cool down and remove impurities; It needs to be filled with adsorbent and placed in the coolant. So what important role can it play in pulse titration experiments? Most metal dispersion tests use hydrogen oxygen titration. When hydrogen reduces oxides, it produces H2O, and the response signal value of H2O in TCD is opposite to the corresponding value of H2 signal, that is, H2O will cancel out the intensity of the remaining H2 signal peak; When the sample does not consume H2, the standard peak is not affected by H2O, resulting in a higher result in calculating the amount of H2 consumed. The final calculated metal dispersion will also be higher, and even the calculated activity specific surface area value will be large and off spectrum.

Figure: Water in a cold trap

② Catalysts supported on carbon, such as palladium and carbon, are prone to "burning". What should be done?

Catalysts supported on carbon materials such as palladium and carbon will experience combustion during the process of oxygen absorption. How should we avoid it during testing? Firstly, it is necessary to reasonably control the oxygen absorption temperature and titration temperature. It is not advisable to have the temperature too high, and room temperature can be chosen if the reaction activity allows. Secondly, if the reaction is not easy at room temperature, low concentration oxygen can be used or pulse injection can be used to control the oxygen content, but the temperature should also be controlled within 100 ℃ as much as possible.

③ How to Conduct Active Metal Dispersion Testing for Metal Ni

The testing of metal Ni often does not require oxygen absorption, which can lead to the failure of the testing experiment. The testing process of Ni should not refer to the testing process of Pt/Pd/Rh and other metals, and the H-O reaction method should not be used. The biggest purpose of this method is to increase the consumption of H2. If the hydrogen consumption is too small and the quantitative ring volume is too large, TCD may not be able to detect it, so many low load precious metal samples use hydrogen oxygen titration. However, for the testing of Ni, it is difficult for the NiO after oxygen absorption to be reduced by H2 or CO, so the method of directly titrating Ni with H2 or CO should be chosen. It is worth noting that the testing of Ni requires a certain temperature, and it is recommended to operate at 100-200 ℃, with some samples even requiring 300 ℃. In actual testing, CO is easier to obtain effective results than H2.

④ How to Conduct the Metal Dispersion Test for Metal Cu

The metal dispersion test of Cu is similar to the testing process of Pt/Pd/Rh and other metals, using H2 titration method. However, due to the multivalent state of metal Cu, it is difficult to determine the stoichiometric coefficient. Therefore, the oxygen absorption process of Cu cannot use oxygen with higher oxidation performance, and N2O with relatively weaker oxidation ability is needed. This gas can only oxidize Cu to one valence at lower temperatures, thereby solving the problem of stoichiometric coefficient. It is recommended to choose the oxidation temperature and titration temperature between 100-200 ℃ in the experiment.

Chapter 8 Precautions

一、Preparation before experiment

1.To use gas correctly, refer to the following table

Target experiment	Carrier gas	Treatment/reaction gas	Pulse gas
NH_3-TPD	N_2 or Ar	Low concentration NH_3（1%-5%）	/
CO_2-TPD	He or Ar	CO_2	/
O_2-TPD	He or Ar	O_2 or low concentration O_2	/
N_2-TPD	He or Ar	N_2	/
O_2-TPO	He/O_2 Mixture（5%-10% O_2）	He or N_2	/
H_2-TPR	Ar/H_2 Mixture（5%-10% H_2）	N_2 or Ar	/
	N_2/H_2 Mixture（5%-10% H_2）	N_2 or Ar	/
CO-TPR	low concentration CO	He or Ar	/
Metal dispersion	N_2 or Ar	N_2 or Ar O_2（optional step）	H_2 or low concentration H_2
Oxygen storage capacity	He	H_2	O_2
Hydrogen storage capacity	N_2 or Ar	O_2	H_2

First, check if the gas circuit connection is correct. After the gas is turned on, set the output pressure to 0.2~0.5MPa, and check if the software and instrument are successfully connected.

2. Correct use of reactors

- The experimental temperature ＜ 600 ℃ using a glass reactor.
- The experimental temperature ＞ 600 ℃, a quartz reactor is used, and the nozzle of the quartz reactor is marked as "1200 ℃".

When installing the reactor, first try to install (compare the position), keep the reactor perpendicular to the ground, and then tighten the nuts; The inlet and outlet nuts should be tightened simultaneously to avoid reactor damage.

3. Properly loading the bed and catalyst

- Quartz cotton should be used as the bed layer, and the top of the bed layer should be flat and level with the bottom of the manifold.
- Install an appropriate amount of catalyst according to the operation manual, and the catalyst should be laid flat on the bed layer, with a general bed height of a few millimeters; If the catalyst is relatively fluffy, the filling height should be less than 1cm; The catalyst should not be too fine, generally not less than 80 mesh.

4. Correct use of four way and six way valves

- Except for pulse experiments, the six way valve switch needs to point towards "**ä**" injection pressure.
- In all experiments, the four-way valve needs to be directed towards“ **↑**”.

5. Correct use of thermocouples

- The temperature detector (thermocouple) should be inserted into the bottom of the manifold.
- When raising the electric furnace, the reactor manifold should be tightly pressed against the furnace wall, and the furnace mouth should be filled with quartz cotton.

6. Correct use of cold hydrazine

- When NH_3-TPD and CO_2-TPD are used, adsorbents such as silica gel cannot be added to the cold hydrazine tube.
- When using H_2-TPR, use a glass cold hydrazine tube, fill the tube with dried discolored silicone, and place a mixture of ice water or liquid nitrogen/isopropanol in a cold hydrazine cup.

7. Install the exhaust pipe correctly

- Exhaust pipes 1-4 should be installed independently and discharged outdoors; Avoid connecting exhaust 1/2 and exhaust 3/4, and do not use the same exhaust pipe.
- When using hazardous gases such as CO, NH_3, H_2, etc., exhaust pipes must be installed and discharged outdoors.
- When using O_2 and H_2 simultaneously, the same exhaust pipe cannot be used.

二、During the experiment

1. During the degassing and adsorption stages, TCD does not need to be activated.
2. When heating up the program, do not touch or shake the high-temperature furnace.
3. To protect the thermocouple and extend its service life, wait until the furnace temperature drops below 200 ℃ before lowering the electric furnace.
4. Start TCD constant temperature in advance, usually at 80 ℃ or 100 ℃; When running the baseline, the reference and test air circuits of TCD must be turned on first, with consistent flow settings, before turning on TCD (i.e. the TCD indicator light is on).
5. Manual operation experiment, after TCD is turned on, let it automatically run for 10-15 minutes, and then manually adjust to zero; Adjust to zero every 2-3 minutes until the requirements are met.
6. During H2-TPR, the coolant (mixture of ice water or liquid nitrogen/isopropanol, etc.) is loaded into a cold hydrazine cup while starting TCD.
7. During the experiment, if there are black/brown/yellow/oily condensate on the reactor tube wall, it may be due to sample decomposition or incomplete treatment. The signal line generated at this time may have interfered with the target signal line, and excessive effluent can contaminate the instrument and cause unnecessary property damage. This situation should be avoided as much as possible before testing. Especially, the sample should not contain untreated organic matter.
8. When using automatic operation mode, after preparing according to the requirements in the operation manual, set the operating parameters correctly.

三、End of experiment

1. After each use of gas, especially corrosive gases such as ammonia and hydrogen sulfide, the main valve and pressure divider valve of the gas cylinder should be closed, and the gas between the gas cylinder and the instrument inlet should be discharged thoroughly, and the gas path should be cleaned with inert gas.
2. After each experiment, all gas between the connected instruments and the gas cylinder should be drained to avoid damaging the valve without the instrument for a long time.
3. After the experiment, the TCD should be turned off first (i.e. the TCD indicator light should be turned off), and then the gas cylinder should be turned off.
4. After the manual test is completed, pay attention to saving the data.

Chapter 9 Common Problems and Solutions

一、Security alarm

1. Combustible gas alarm

The high-frequency and urgent alarm sound of "di di di di".

2. High temperature safety alarm

“di~~di~~di~~di~~” Low frequency alarm sound with a certain time interval。

二、Signal line faults and troubleshooting methods

1. **The signal line is always drifting in a certain direction and cannot be stable**

(1) Determine whether the flow rate of the No. 2 mass flow meter is normal. If it is not normal, check the operation status of valve 7. After normal operation, if the flow rate is still abnormal, check whether the gas circuit is "blocked". When the No. 2 flow meter is operating normally, it is necessary to check the working status of valve 8. (First, ensure that the operation of the No.1 flow meter is normal)

(2) Due to the presence of air leakage in a certain pathway, this situation often occurs in the testing gas path. Specific exclusion methods refer to.

Summary: The occurrence of this problem is mainly caused by two reasons: firstly, there is no gas in one of the two channels of TCD, and secondly, there is gas leakage in one of the channels or the presence of effluent in the sample.

2. Irregular shaking (burrs) of the signal line

(1) If the intake pressure is unstable, replace the pressure reducing valve and pressure stabilizing valve to eliminate it.
(2) The air outlet is blocked and blocked. Check whether there are foreign matters at the outlet of the exhaust pipe and in the exhaust pipe. Raindrops in rainstorm weather will cause poor exhaust, and this phenomenon will also occur.
⑶ TCD pollution, this problem requires the use of gas to clean the TCD gas circuit. After blowing, open the TCD heating device, first raise the temperature to 200 ℃ and blow for 20 minutes, then lower the temperature to 100 ℃ and blow for 2 hours. If the TCD signal still cannot be stable during the constant temperature process, it is recommended to replace the TCD. Note: To clean TCD, it is necessary to ensure that there is always gas passing through the reference and test gas paths, and the flow rate can be set to 80-90ml/min.

3．**The peak shape is not smooth and has serrations**

(1) Determine the signal strength (peak voltage value). If the signal strength is relatively weak (1-2mv), this phenomenon is normal. If the signal value is high and there is still this phenomenon, it is likely due to sample decomposition or the influence of ejected substances. Try to remove it through cold well as much as possible
(2) Empty the sample tube and run the baseline. If the baseline is stable, it can be determined that it is a sample problem. If it is abnormal, check for air leakage and use gas to clean the TCD.

三、 Non peak faults and troubleshooting methods

1. Check the working status of the four way valve and confirm that the position of the four way valve is "up" and not in the "empty" state.

排空状态

工作状态

2. Check the coordinates of the software's horizontal axis. If the coordinates are reduced too much, make changes. The first scale on the "0" coordinate is 5-10mv.
3. Check if the test gas is reasonable, such as using a mixture of argon and hydrogen gas for tpr testing, which cannot be done using pure hydrogen gas; The carrier gas for O2-tpd should be argon or helium, and nitrogen cannot peak (the thermal conductivity coefficient of nitrogen and oxygen is too close, and the TCD detector cannot separate the signal).
4. Check the working status of TCD and whether the air circuit is normal.

Note: Confirm that TCD is in the on state (the indicator switch light is red); Check if the test air circuit is correct, manually click on each valve to confirm if the valve is working properly. The common problem is that valve 8 is not switched to the TCD test outlet; Check if the output flow rate of the mass flow meter is normal and make adjustments to confirm that the flow meter is working properly and does not experience a "dead state".

Correct operation method for TCD temperature control:

A. Enable TCD

B. Long press and hold the 'run' button until the run indicator light turns green

C. Press the up/down keys to set the constant temperature, usually set to 80 ℃

Attention:

- Before turning off TCD, first turn off the TCD temperature control (i.e. press and hold the "run" button until the run indicator light goes out), and then turn off TCD
- Except for commonly used temperature control buttons, do not press other control buttons indiscriminately; If the garbled code is pressed, you can wait for a few minutes until the garbled code on the temperature control meter disappears before continuing the operation.

5. Check if the use of the cold trap is correct. NH3-TPD cannot add adsorbents to the cold trap, and the desorbed NH3 will be adsorbed by the adsorbent without detecting a signal; In TPR testing, reaction products such as H2O, CH4, and HCl often "cancel" or even "negative" signal peaks, which requires the addition of adsorbents in the cold trap tube to drive them away.

四、 Reasons for non peak separation and improvement methods

1. The heating rate is too fast, resulting in a "hump" and unclear separation of the two peaks. It is necessary to reduce the heating rate, but not too much.
2. The heating rate is too slow, resulting in insufficient "sharpness" and too flat and wide peaks. It is necessary to increase the heating rate appropriately.
3. If the peak temperatures of the two signal peaks are too close and the consumption or removal amount is large, resulting in peak superposition, it is necessary to increase the carrier gas flow rate.

Note: If the above methods cannot be solved, more reliable data can only be obtained through external mass spectrometry detection.

五、Heating fault and troubleshooting methods

1. Software error 'Thermocouple damaged or not placed in designated location'

(1) Programmed heating furnace not placed in designated position or damaged

Due to the self inspection program set by the software, the electric furnace was not placed correctly. The software controls the continuous power supply to the electric furnace, and if the temperature does not rise or fall, the software will determine a fault.

(2) The heating program has not ended, remove the programmed heating furnace.

(3) Thermocouple damage

If the thermocouple is damaged, the software will display a temperature of 1024 ℃. If the display is normal, the thermocouple can be observed for temperature changes by measuring its body temperature when the temperature is displayed as room temperature.

(4) Programmed heating furnace damaged

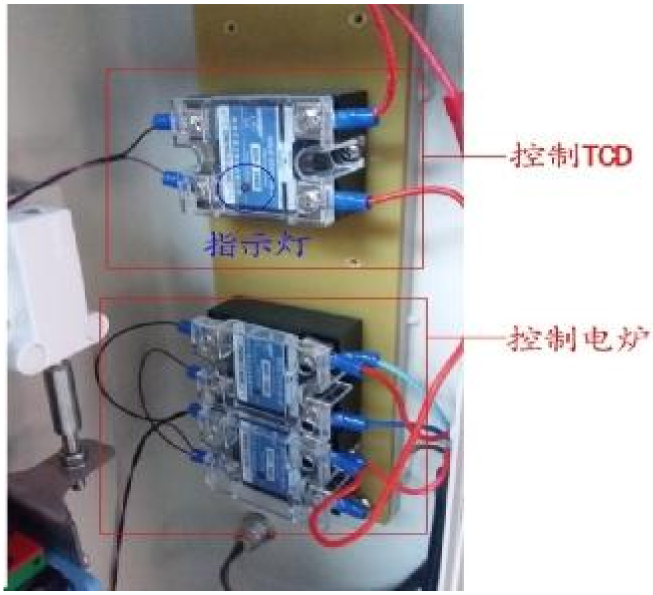
The electric furnace needs to use a "multimeter" to measure whether there is resistance (whether it is damaged), and if it is damaged, replace the programmed heating electric furnace.

(5) Motherboard fault: After setting the heating program, the motherboard indicator light does not flash.

PS: After power on, the green light remains on. When not in working mode, the blue light slowly flashes (in the "one exhale, one inhale" state); During normal operation, the blue light flashes frequently.

(6) Relay failure

The motherboard indicator light is working normally, and the relay's working indicator light is not flashing.



2. Poor control of program heating rate

It can be adjusted by adjusting the height of the programmed heating electric furnace (which can be appropriately lowered or raised by 0.3-0.5cm). If it cannot be improved, the electric furnace needs to be replaced.

3．**The heating curve jumps up and down in the high temperature range (blue line)**

Thermocouples are damaged or cannot operate at high temperatures (often after 700 ℃)

六、TCD faults and troubleshooting methods

1. TCD constant temperature does not work

(1) Run the temperature control meter and check if the relay is working properly. If the indicator light does not flash, replace the relay. If the relay is working properly, it indicates that the heating device is damaged.

(2) The temperature control meter displays HHHH, and the temperature measurement pt resistance is damaged

2. The TCD work indicator light does not light up

(1) TCD switch damaged

(2) Damaged power supply

(3) The polarity switch is not placed in the correct position

七、Electromagnetic valve faults and troubleshooting methods

1. Damage

When the software is online normally, "click" the control button, and the solenoid valve has no "action" (no sound). It is necessary to open the solenoid valve to confirm whether the solenoid valve is damaged or contaminated. For a two-way solenoid valve, there is no obvious damage or pollution after opening, and it needs to be installed before control. To eliminate the problem of long inactivity and "membrane" jamming, if it still cannot be controlled, the control position of the solenoid valve on the motherboard needs to be changed, Troubleshooting the motherboard; In addition to the above issues, there are also issues with the two position three-way solenoid valve, such as "gas leakage" caused by the position change of the valve core during disassembly and assembly, and the inability to switch the gas path. The reason for not switching the gas path is because the valve core position is not close to the relative suction surface, and the valve core needs to be "knocked" back to the sealing surface; The main reason for "gas leakage" is that the position of the valve core exceeds the sealing surface and is uneven, and it needs to be repositioned by tightening the top joint; The most corroded and damaged solenoid valve is the "No. 8" valve, which first manifests as an abnormal TCD signal line. Therefore, TCD problems should be first investigated for valve No. 8 fault

2. Pollution

The solenoid valve is a detachable and cleanable "diaphragm" type solenoid diaphragm and gasket during disassembly and cleaning; After cleaning, please confirm that the air circuit is unobstructed. If necessary, it needs to be cleaned repeatedly to confirm the cleanliness of the air circuit.

Chapter 10 Instrument Accessories

一、Attachment Table

序号	编码	名称	规格
1	2600-PCA-01	Electric furnace	1200℃
2	2360-PW-120	Furnace power cord	40cm
1	1330-LN-04	Cold trap	400ml
3	1220-GAS-3163	nal gas pipeline	3 meters/piece
4	1220-GAS-PE10	Air hose	10 meters/piece
5	2100-M-3	Φ3 Sealing ring	2.2x1.9
6	2100-M-6	Φ6 Sealing ring	5x2.5mm
3	2100-M-10	Φ10 Sealing ring	8.75x3.05
7	2150-M-M8*3	Gas pipeline lock catch	M8*3
8	2010-U-1200	High-temperature reactor	1200℃
9	2010-U-600	Low-temperature reactor	600℃
10	2020-L-240	Funnel	240mm
11	2230-SH-270	Sample hook	270mm
12	2350-K1-1200	thermocouple	1200℃
13	2350-K1-600	thermocouple	600℃
14	2330-PW-200	Power cord	1.5m
15	2340-PW-210	Patch panel	220V10A
16	2320-USB-1.8	Data cable	1.8m
17	2060-M-1200	Quartz Wool	10um
18	2400-PC-1T	Computer	random

二、Attachment Introduction

（一）Sealing accessories for gas pipeline, as shown in Figure 8.2.1; The exhaust pipe is shown in Figure 8.2.2

Figure 8.2.1

Figure 8.2.2

（二） Sampling and loading accessories

1. Reactors:

mainly divided into two types: low-temperature reactors and high-temperature reactors. When the experimental temperature exceeds 600 ℃, a high-temperature reactor must be used. The outer wall of the high-temperature reactor is marked with the words "1200 ℃". As shown in Figure 8.2.3

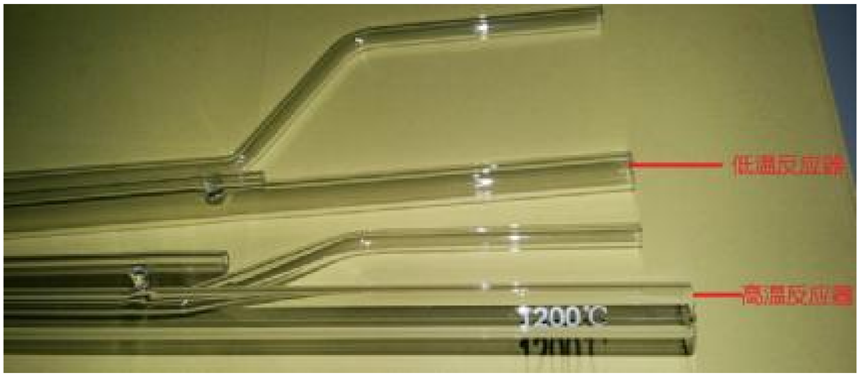


Figure 8.2.3

2. Reactor and sample loading accessories, as shown in Figure 8.2.4;
   Reactor installation accessories, as shown in Figure 8.2.5

Figure 8.2.4

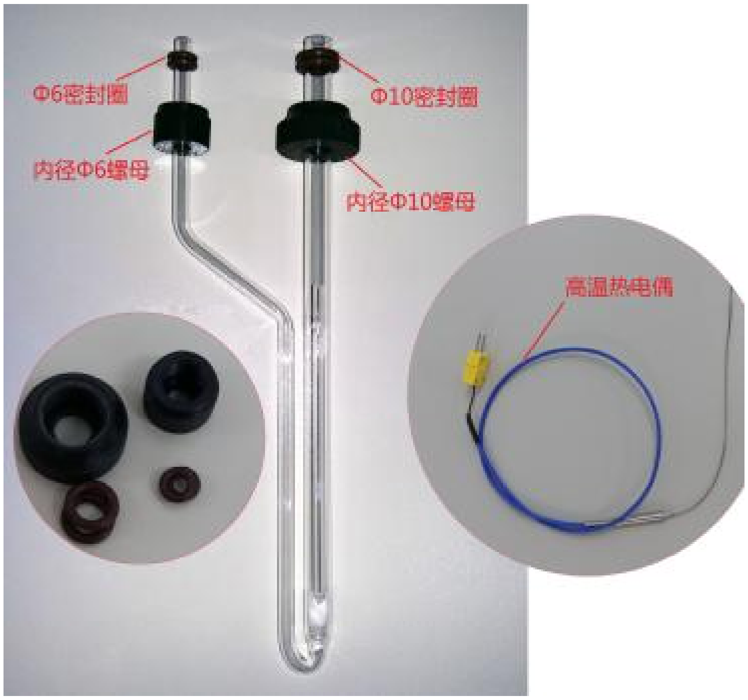
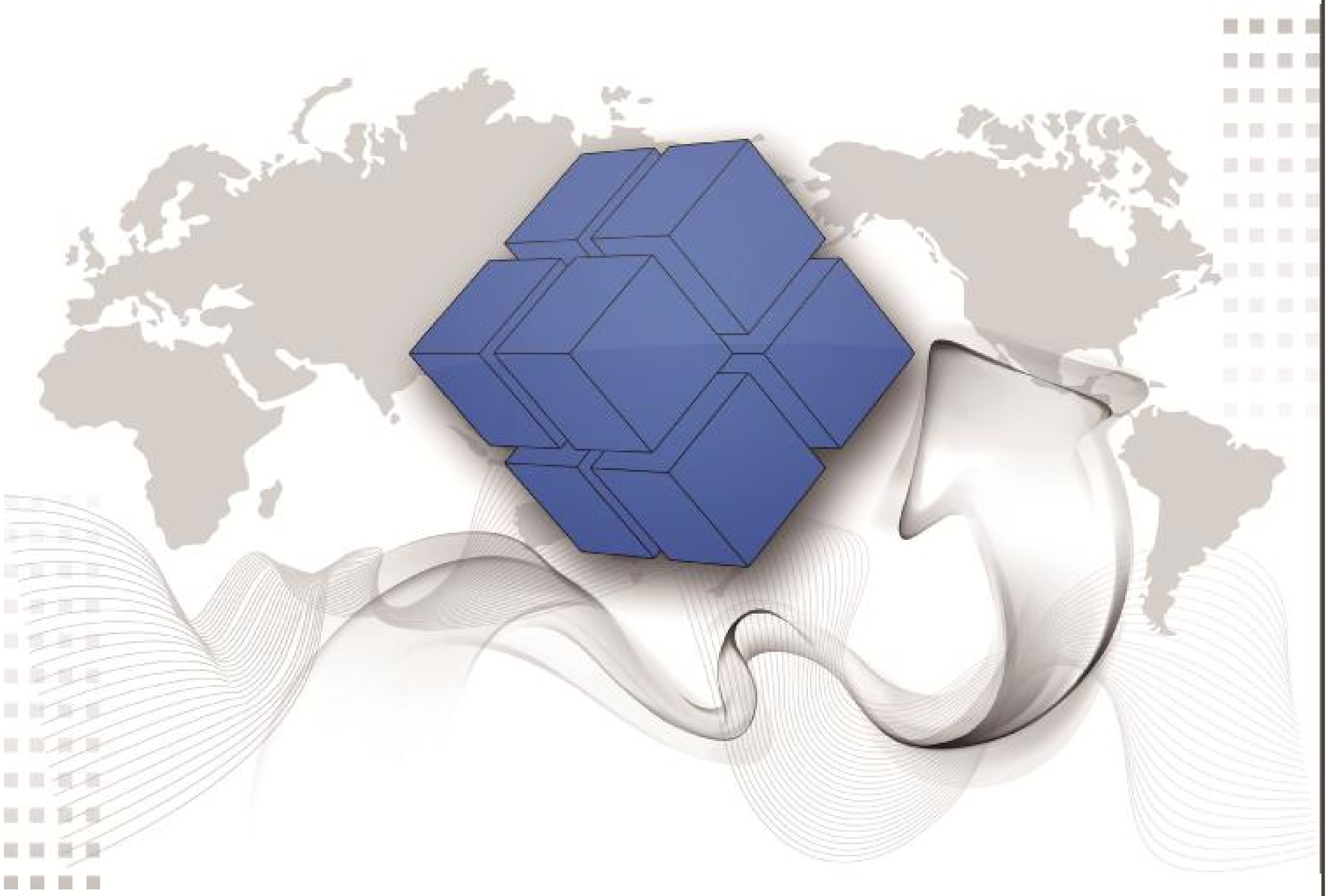


Figure 8.2.5

（三） Host and other accessories, as shown in Figure 8.2.6

Figure 8.2.6



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