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Y/composite titania-silica (CTS) supported catalyst for hydrotreating coker gas oil

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Abstract

Y/composite titania-silica (CTS) support was prepared by the in situ growth of CTS on HY zeolite. The effects of HY zeolite pretreatment and Y/CTS modification with P and F for adjusting the acidity of the support were studied. The results showed that the structure of Y/CTS was in the form of CTS as shell and HY zeolite particles as core. The content of HY zeolite affected the acidity, acidity distribution and pore structure of Y/CTS. The density of strong acid sites on the HY zeolite surface could be partly reduced by dealumination with citric acid. This reduced the CTS coverage on the outer surface of the HY zeolite, leading to the increased acidity of Y/CTS. The acidity distribution of the support could also be adjusted by P and F modification. Hydrotreating catalysts were prepared with Y/CTS as support. The catalysts were tested using the hydrotreating reaction of a coker gas oil (CGO). The experimental results showed that the catalyst hydrodenitrogenation (HDN) performance could be remarkably improved by adjusting the acidity of the catalyst support via HY zeolite pretreatment and P and F modification. The catalysts with proper Brönsted (B) acidity and Lewis (L) acidity behaved well in hydrodesulfurization (HDS) and HDN performances.

Keywords: Coker gas oil; Hydrotreating; Catalyst; Composite support; Acidity

1. Introduction

In recent years, the demand for light oils has been steadily increasing, while the source of light oil has been deceasing. Therefore, it is necessary to produce more valuable hydrocarbons from undesirable feedstocks such as coker gas oil (CGO), coal derived oil and shale oil [1]. However, these feedstocks, especially CGO, contain large amount of heteroatoms such as S, N and so on. Because these heteroatom-containing compounds give rise to serious problems such as coke deposition and poisoning for fluid catalytic cracking (FCC) and hydrocracking catalysts. Therefore, hydrotreating that removes heteroatoms from these feedstocks is of great importance for upgrading these undesirable feedstocks to valuable products. By this way, S and N contents in CGO are reduced and therefore their poisoning effects on cracking catalysts are lessened; poly-aromatics are partly saturated, the crackability of the feedstock can be improved, and coke deposition is reduced; light oil yields are increased and their quality can be greatly improved. During a typical CGO hydrotreating process, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrogenation of aromatics take place. Generally, an ideal CGO hydrotreating catalyst should have large pore diameter and proper acidity intensity and distribution to meet the requirements of the diffusion and reaction of large CGO molecules [2].

Composite titania-silica (CTS) has large pore diameter, large pore volume, and high specific surface area and thus is suitable to be used as the support of CGO hydrotreating catalysts. However, the acidity of CTS is not strong enough for CGO hydrotreating reactions. Herein, HY zeolite is selected to adjust the acidity and pore structure of CTS, the effects of HY zeolite pretreatment and modification with P and F on support acidity were studied, and the catalytic hydrotreating performance of the resulting catalysts was assessed.

2. Experimental

2.1. Preparation

CTS-*n* preparation. The sol–gel method was used to prepare CTS-*n* (*n* is the atom ratio of Ti to Si in composite) [3]. Solution

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A was prepared by dissolving desired amounts of tetrabutoxytitanium (TBOT) and tetraethoxysilane (TEOS) into ethanol separately and then mixing the resulting solutions homogeneously. Solution B was obtained by mixing desired amounts of water, acetic and ethanol. Under strong magnetic stirring, solution B was dropwise added to solution A. After being stirred for 15 min, the sol obtained was aged at room temperature for 24 h to form a titania-silica gel, and then the gel was dried by supercritical CO_2 fluid drying for 3 h and white particles were obtained. After 3 h of calcination at 500 °C in air, the particles of 20–40 meshes in size named as CTS-*n* were selected as catalyst support.

Y/CTS-*n* preparation. An in situ growth method was developed to obtain composite support Y/CTS-*n*. By homogeneously dispersing HY zeolite powders or modified HY zeolite powders into solution A and using the preparation procedure described above, composite Y/CTS-*n* supports with HY or modified HY as core and CTS-*n* as shell were obtained by the overgrowth of CTS-*n* on the outer surface of HY zeolite particles or modified HY particles. The post-treatment methods of the resulting composites are identical to those used for CTS-*n*.

Acidity modification of Y/CTS. In order to understand the effect of the catalyst acidity on hydrotreating performance, two methods were adopted to adjust acidity of the composite supports. The first one is to pretreat HY with citric acid. 25 g of HY zeolite dispersed into 0.05 mol/L citric acid solution and placed quietly at 35 °C for 1 h, and then filtered and washed with deionized water for three times, and finally dried at 120 °C for 3 h. The second method is to introduce acidic components P and F into the composite supports by impregnating the support with $(NH_4)_2HPO_4$ and NH_4F aqueous solutions. The composite supports were impregnated firstly at 60 °C for 2 h, then dried, and finally calcined to obtain the modified supports with different contents of F and P via adjusting the concentrations of the $(NH_4)_2HPO_4$ and NH_4F aqueous solutions.

Catalysts preparation. Firstly, the supports were impregnated with nickel nitrate aqueous solutions by the equal volume impregnation method at room temperature for 4 h, dried at 120 °C for 3 h and calcined for 3 h at 500 °C. Then, the supports loaded with Ni were impregnated with an ammonium para-tungatate aqueous solution at room temperature for 4 h, dried at 120 °C for 3 h and calcined for 3 h at 500 °C to obtain NiW hydrotreating catalysts.

2.2. Characterizations

The specific surface area, pore volume and pore diameter of the supports and the corresponding catalysts were measured on a Micromeritics ASAP-2400 instrument by BET method. Prior to measurement, the samples were degassed under the conditions of 1.6 Pa and 200 °C for 4 h.

The Brönsted (B) and Lewis (L) acidity of the samples were analyzed on a MAGANA 560 FT-IR instrument by pyridine adsorption method. After the samples being purified at 350 °C for 2 h and cooled down to room temperature, pyridine adsorption was performed. The pyridine was desorbed by temperature programming desorption (TPD), and the data were recorded at 200 °C and 350 °C, respectively.

The acidity amount was analyzed on a TP-5000 multifunction adsorption instrument by NH_3–TPD. The catalyst was treated in air at 500 °C for 1 h, after the sample was cooled to 120 °C, NH_3 was absorbed for 30 min, and then the temperature was raised to 750 °C at 10 °C/min. The signal is recorded by a mass spectrograph.

The X-ray diffraction (XRD) patterns of the HY zeolite and citric acid treated HY zeolite (CY zeolite) were obtained on a DMAX-2400 polycrystalline powder diffraction instrument and the wavelength of the light-source was 1.54 nm. The working voltage and electric current of the cube target X-ray tube are 40.0 kV and 100.0 mA, respectively.

The contents of S and N in the CGO were determined on an ANTEK 7000 N/S analyzer by the method of ultraviolet florescent spectroscopy.

2.3. Hydrotreating performance of catalysts

The hydrotreating performance of the catalyst was evaluated on a JQ-III hydroprocessing unit, and a commercial CGO sample was chosen as feedstock. The contents of S and N in the CGO are 11644 $\mu g\ g^{-1}$ and 8840 $\mu g\ g^{-1}$, respectively. The catalyst loading was 3 mL. The reaction conditions were 380 °C, 6.0 MPa, 1.0 h^{-1} liquid hour space velocity (LHSV), and volumetric ratio of hydrogen to oil was 1000. The catalyst presulfidation conditions are as follows: the presulfidation solution 2 wt.% CS_2/cyclohexane, 300 °C, 4.0 MPa, 6 h^{-1}, and 4 h.

3. Results and discussion

3.1. Characterization of CTS-*n*

Table 1 lists the specific surface areas and pore volumes of CTS-*n*, and Fig. 1 shows the nitrogen adsorption isotherms of CTS-1 and CTS-4. It can be found that CTS-*n* have large specific surface areas, pore volumes and mean pore diameters and thus are profitable for the defusing of large molecules of CGO.

For CTS-*n* to be used as an excellent CGO hydrotreating catalyst support, not only large specific surface area and pore volume but also proper acidity is required [4]. Table 2 lists the acidity of CTS-*n* of various Ti/Si atom ratios measured by pyridine adsorption, and Fig. 2 is the IR spectra of absorbed pyridine of CTS-*n*. The acidity of titania (TiO_2) and silica

Table 1
Specific surface area and pore volume of CTS-*n*

Sample	Specific surface area ($m^2\ g^{-1}$)	Pore volume ($ml\ g^{-1}$)
CTS-0.25	525	1.93
CTS-1	437	1.39
CTS-4	222	0.50
CTS-8	229	0.63

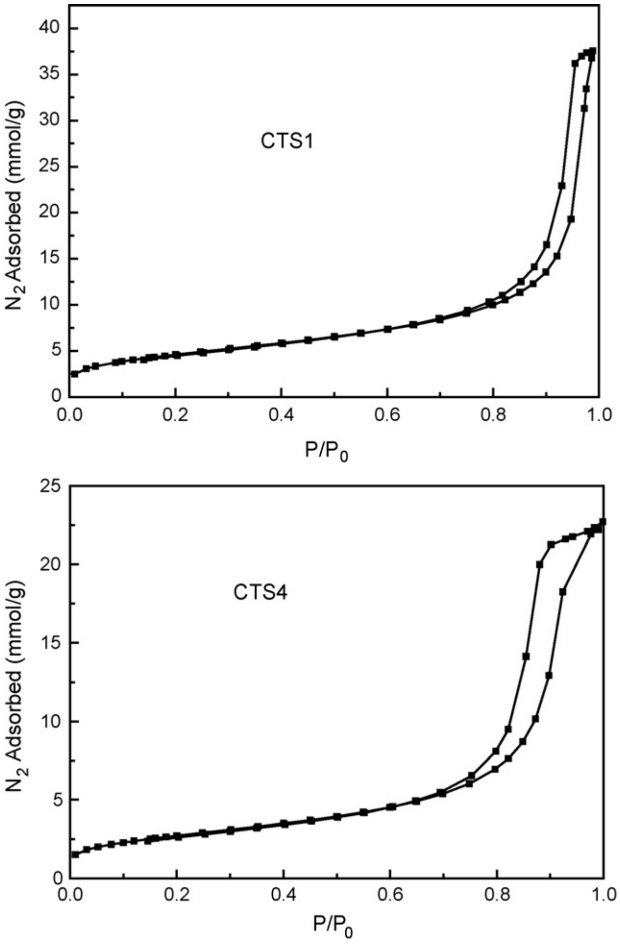

Fig. 1. N_2 adsorption Isotherms of CTS-1 and CTS-4.

(SiO_2) are also included in Table 2 for comparison purpose. It shows that pure TiO_2 has only L acidity, while SiO_2 does not show any acidity, CTS-*n* contains higher L acidity and produces B acidity compared with TiO_2. In these samples, CTS-4 has the highest L acidity and the total acidity amount, whereas CTS-1 has the largest proportion of B acidity. Consequently, CTS-1 and CTS-4 were selected for the further investigation.

Table 2 and Fig. 3 show the acidity density and acidity distribution of CTS-1 and CTS-4. It can be seen that although the total acidity of CTS-4 is less than that of CTS-1, the proportion of medium and strong acidity of CTS-4 is higher. For medium and strong acidity plays more important role than weak acidity during CGO hydrotreating reactions [5], CTS-4 is selected for further investigation.

Table 2
Brönsted and Lewis acidity of CTS-*n* with various Ti/Si atom ratios

Sample	L	B	L + B	B/(B + L)%
TiO_2	2.0	0	2.0	0
CTS-4	6.5	1.5	8.0	18.7
CTS-1	5.0	1.7	6.7	25.4
CTS-0.25	4.2	0.8	5.0	16.0
CTS-0.125	2.8	0.4	3.2	12.5
SiO_2	0	0	0	–

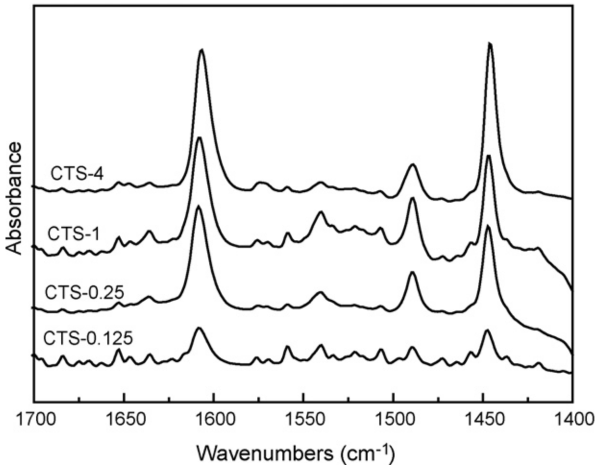

Fig. 2. IR spectra of absorbed pyridine of CTS-*n*.

3.2. Characterization of Y/CTS

Fig. 4 shows the SEM micrographs of the HY zeolite, CTS-4 and Y/CTS and the TEM imagines of Y/CTS. It can be found that the formed Y/CTS is a new shell-core structure. CTS-4 is evenly covered on the outer surface of the HY zeolite particles. This kind of structure provides the gradient pore diameter and acidity distributions resulted from microporous HY zeolite with stronger acidity and mesoporous CTS-4 with weaker acidity. It will be favorable for the diffusion and replay-type reaction of large CGO molecules.

Table 3 lists the specific surface areas, pore volumes and pore diameters of *m*Y/CTS (the prefix m denotes *m*% of HY zeolite in Y/CTS). With the increasing content of HY zeolite in Y/CTS, the specific surface area and pore volume of Y/CTS increases and the pore diameter changes slightly. But the pore volumes and pore diameters of Y/CTS were smaller compared with those of CTS-4.

Table 4 lists the acidity of *m*Y/CTS. When *m* is smaller, the total acidity amount of *m*Y/CTS was less than that of CTS-4 and HY zeolite. With the increasing *m*, the total acidity amount

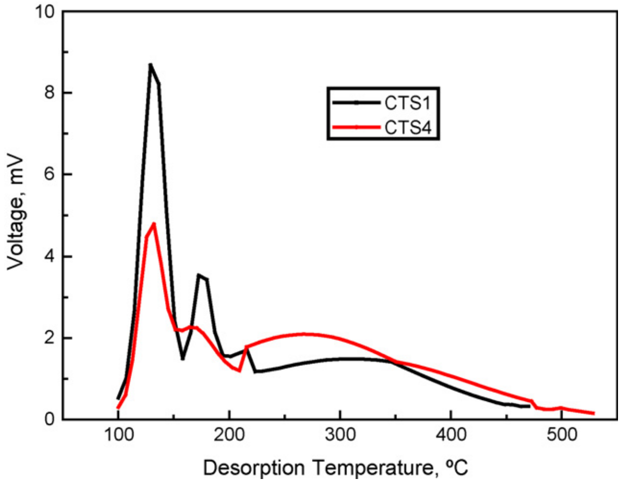

Fig. 3. NH_3–TPD profiles of CTS-*n*.

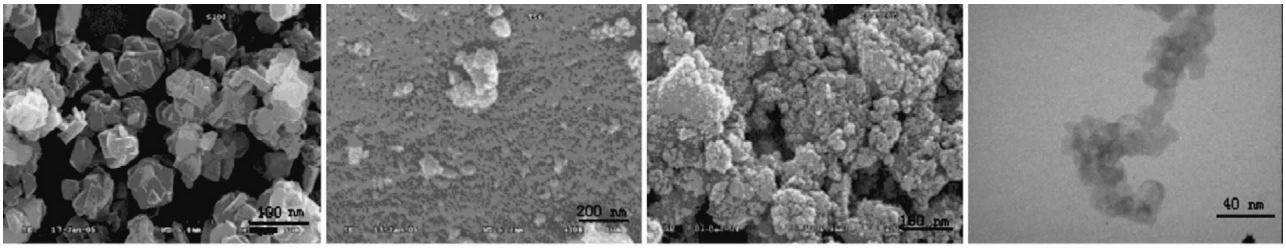
HY SEM CTS4 SEM Y/CTS SEM Y/CTS TEM

Fig. 4. SEM and TEM micrographs of the supports.

of mY/CTS increases. When m rises up to 20, the total acidity amount of mY/CTS exceeds that of CTS-4, but still less than that of HY zeolite. As for acidity types, both B and L acidity densities increase with the raising of m value, herein B acidity increases in a smaller range than that of L acidity. This may be due to the strong B acidity sites on the surface of HY zeolite particles induce the growth of CTS. So, when the content of HY zeolite was low, the total acidity density of Y/CTS was lower than that of CTS-4 and HY zeolite. With the increasing content of the HY zeolite in Y/CTS, the distribution of the HY zeolite in Y/CTS became less uniform. At the same time, the number of the growing center of CTS-4 increased, the HY zeolite particles could not be totally covered, so the total acidity density rose to be larger than that of CTS-4 under certain conditions, but never exceeded that of the HY zeolite.

Table 4 shows that the acidity density of Y/CTS was not notably higher than that of CTS-4. The possible reason is that the exposed strong B acidity sites of HY zeolite could make the CTS-4 centrally grow on them, so some of them were covered and could not be detected. Therefore, pretreating of HY zeolite to reduce the density of strong B acidity sites on the surface may change the structure and acidity distribution of Y/CTS.

Table 3
Specific surface area, pore volume and pore diameter of Y/CTS

Sample	Specific surface area $(\mathrm{m}^2\,\mathrm{g}^{-1})$	Pore volume $(\mathrm{cm}^3\,\mathrm{g}^{-1})$	Pore diameter (nm)
HY zeolite	713	0.40	2.3
CTS-4	222	0.82	14.5
5Y/CTS	158	0.44	11.1
10Y/CTS	221	0.64	11.7
20Y/CTS	259	0.76	11.7
30Y/CTS	302	0.85	11.3
40Y/CTS	372	0.51	9.3

Table 4
Acidity of Y/CTS with various content of HY zeolite

Sample	Acidity $(\mathrm{A\,cm}^2\,\mathrm{g}^{-1})$					
	200 °C			350 °C		
	B	L	B + L	B	L	B + L
HY	21.6	5.5	27.1	3.1	1.1	4.2
CTS	1.5	6.5	8.0	0.3	0.9	1.2
5Y/CTS	0.9	3.2	4.1	0.1	0.1	0.2
10Y/CTS	2.7	2.7	5.4	0.3	0.2	0.5
20Y/CTS	3.8	6.4	10.2	0.6	0.6	1.2

3.3. Characterization of CY

HY zeolite was pretreated into CY with the method of citric acid dealuminum [6]. Table 5 lists the specific surface areas, pore volumes and pore diameters of HY zeolite and CY zeolite. Compared with HY zeolite, CY zeolite has higher specific surface area, but has approximately the same pore volume and pore diameter. It indicates that the degree of dealuminum was low and the crystal structure of the HY zeolite was not destroyed obviously.

In order to further illustrate the variation of CY from HY zeolite, XRD characterization was carried out (shown in Fig. 5) and their atomic ratios of Si/Al, cell numbers, and crystallinities were calculated (shown in Table 6). Here, the crystallinity of the HY zeolite was assumed to be 100%. Fig. 5 shows that the characteristic peaks of HY and CY zeolite do not obviously deviate from each other and there is no peak for impurity. This result indicates that the crystalline structure was well retained and the atomic ratio of Si/Al and the cell number changed inconspicuously.

Further investigation was carried out to study the effect of the citric acid pretreatment on HY zeolite acidity. Table 7 gives the acidity characterization results of the HY and CY zeolites. It shows that the acidity density of the HY zeolite was reduced after being pretreated. This is because that a certain amount of aluminum is being dissolved from the structure of the HY zeolite and caused the reduction of acidity especially that of strong B acidity.

Table 5
BET characterization of HY zeolite and CY zeolite

Character	HY zeolite	CY zeolite
Specific surface area $(\mathrm{m}^2\,\mathrm{g}^{-1})$	714	753
Pore volume $(\mathrm{cm}^3\,\mathrm{g}^{-1})$	0.40	0.41
Pore diameter (nm)	2.3	2.3

3.4. Characterization of CY/CTS

Table 8 lists the specific surface areas, pore volumes and pore diameters of the composite support CY/CTS and Y/CTS. Here, CY/CTS is a support made from CY and CTS-4. The content of HY and CY zeolite in the support is 10%. Table 8 shows that the pretreatment of HY zeolite has little effect on the specific surface area of Y/CTS. But the total acidity amount (B and L) of CY/CTS was higher than that of Y/CTS (shown in

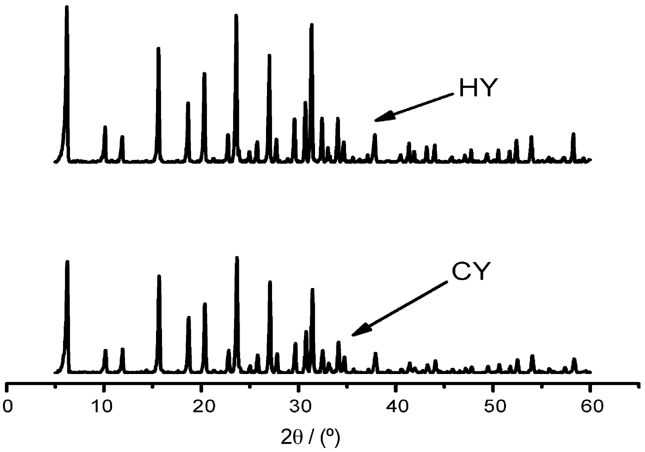

Fig. 5. XRD patterns of HY and CY.

Table 6
Characterization of HY and CY

Character	HY	CY
Cell number (nm)	2.4649	2.4648
Crystal degree (%)	100	94.92
Atomic ratio of Si/Al	5.00	5.28

Table 7
Acidity characterization of HY and CY

Sample	Acidy (A cm^2 g^{-1})					
	200 °C			350 °C		
	B	L	B + L	B	L	B + L
HY	21.6	5.5	27.1	3.1	1.1	4.2
CY	18.1	2.2	20.3	2.4	1.0	3.4

Table 9). Due to the pretreatment of HY zeolite, the strong B acidity density of the Y/CTS was reduced, while the strong L acidity density increased. It can be concluded that the acidity density of Y/CTS can be adjusted by the pretreatment of HY zeolite. The reduction of strong B acidity sites of HY zeolite can restrain the coverage of CTS on the acid sites of the HY zeolite particles.

3.5. P and F modification of the composite support

The previous researches [7–16] showed that P and F elements can alter the acidity density and acidity distribution of the support, improve the dispersion and modify the state of the active metal; they can also impact the pore structure of the support to a certain extent. However, no information on the P and F modification of composite oxides has been reported.

Table 8
The BET characterization of Y/CTS and CY/CTS

Sample	Specific surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
Y/CTS	221	0.64	11.7
CY/CTS	228	0.61	11.4

Table 9
Acidity characterization of Y/CTS and CY/CTS

Sample	Acidity (A cm^2 g^{-1})					
	200 °C			350 °C		
	B	L	B + L	B	L	B + L
Y/CTS	2.7	2.7	5.4	0.3	0.2	0.5
CY/CTS	4.9	4.8	9.7	0.2	0.4	0.6

3.5.1. P modification of Y/CTS

The improvement of catalyst hydrotreating performance due to the addition of P can be attributed to the following factors [7–12]: the dispersion of the active metal can be improved and acidity density can also be adjusted by means of the interaction alteration between the active metal and the support; the proper acidity distribution enhances the adsorption of nitrogen-containing compounds on the active sites and accelerated the rupture of C–N bond, which leads to the improvement of catalyst HDN performance.

Y/CTS modified by 1–5 wt.% P were designated as 1PY/CTS, 2PY/CTS, 3PY/CTS, 4PY/CTS, and 5PY/CTS.

Table 10 lists the BET characterization results of P modified supports, and Fig. 6 shows their pore diameter distribution profiles. The results indicate that the specific surface area, pore volume and pore diameter of Y/CTS were slightly affected by P modification. Thus, it can be found that the pores of the support were not seriously blocked by P addition within the investigated P content. However, dual-pore diameter distribution of the support is observed after P modification, with pores centralized at 6.3 nm and 18.6 nm (shown in Fig. 6), while the pore diameter of unmodified support is centralized at about 15 nm. With the increasing content of P in the supports, the pore volume of pores centralized at 6.3 nm decreased and that of 18.6 nm increased.

Table 11 lists the acidity of the support modified with P. It can be found that the density of B acidity and L acidity increased with the increasing content of P. When the content of P is above 2 wt.%, the density of strong B acidity and the

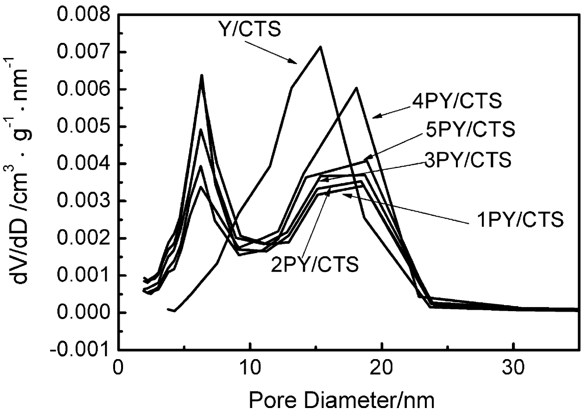

Fig. 6. Pore distribution of Y/CTS modified with P.

Table 10
BET characterization of the supports modified with P

Sample	Specific surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (nm)
Y/CTS	221	0.64	11.7
1PY/CTS	240	0.63	10.4
2PY/CTS	228	0.62	10.9
3PY/CTS	218	0.63	11.5
4PY/CTS	214	0.67	12.5
5PY/CTS	200	0.61	12.2

medium and strong L acidity increased but medium B acidity decreased. So, the acidity distribution of the support can be altered as a consequence of P modification.

3.5.2. *F modification of Y/CTS*

F is often used to modify the hydrotreating catalyst support, too. The main functions of F are [13–17]: (1) F can attract the electrons from the metal atom neighbors, leading to the active metal atoms in the state of lacking electrons, so that the metal is easier to be transformed into active metal sulfide; (2) F atom attracts electrons from nitrogen atoms of nitrogen-containing compounds, so that the C–N bond becomes weaker and the probability of the rupture of C–N bond is increased; (3) F atom can affect the acid sites of the support and alter its acidity distribution.

Y/CTS modified by 1–5 wt.% F were designated as 1FY/CTS, 2FY/CTS, 3FY/CTS, 4FY/CTS, and 5FY/CTS.

Table 12 lists the BET characterization results of the F modified supports, and Fig. 7 shows the pore diameter distributions of these supports. They show that F modification did not have obvious influence on the specific surface area, pore volume and pore diameter of the support. Fig. 7 reveals that the pore diameter of the F modified supports is centralized at two dimensions, 6.3 nm and 18.6 nm. With the increasing amount of F addition into the support, the average pore diameter shifts to the positive direction of the horizontal axis. The reason for the two dimensions of the pores to come into being after the support was impregnated with F and P needs to be further studied in future.

Table 13 lists the acidity of the F modified support. It is found that the density of B acidity was reduced and L acidity was increased to a maximum at first and then fell down later with the increasing F addition.

Table 11
Acidity distribution of the supports modified with P

Sample	Acidity (A $cm^2\ g^{-1}$)					
	200 °C			350 °C		
	B	L	B + L	B	L	B + L
Y/CTS	2.7	2.7	5.4	0.3	0.2	0.5
1PY/CTS	2.4	5.6	8.0	0.2	0.2	0.4
2PY/CTS	3.6	8.2	11.8	1.7	0.4	2.1
3PY/CTS	3.5	7.5	11.0	1.1	0.2	1.3
4PY/CTS	3.3	10.1	13.4	1.6	0.3	1.9
5PY/CTS	3.1	7.1	10.2	1.1	0.2	1.3

Table 12
BET characterization of support modified with F

Sample	Specific surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (nm)
Y/CTS	221	0.64	11.7
1FY/CTS	240	0.74	12.4
2FY/CTS	220	0.75	13.7
3FY/CTS	202	0.71	14.1
4FY/CTS	180	0.64	14.1
5FY/CTS	170	0.67	12.5

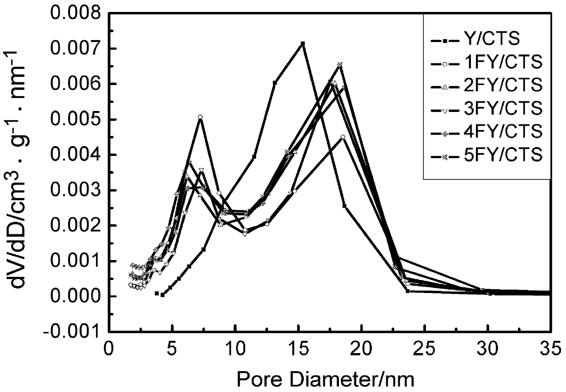

Fig. 7. Pore distribution of Y/CTS modified with F.

3.6. *Influences of the various acidity alteration methods on the hydrotreating performance of the catalyst*

3.6.1. *Influence of HY zeolite content*

Figs. 8 and 9 show the HDS and HDN conversions of the catalysts based on Y/CTS with various amounts of HY zeolite. From the two figures, it can be seen that the HDS and HDN conversions of the catalysts had the similar changing trend with the increasing amount of HY zeolite. Among the evaluated catalysts, NiW/10Y/CTS had the best catalytic performance, with the HDS conversion higher than that of NiW/CTS and the HDN conversion equal to that of NiW/CTS. When the content of HY zeolite was higher than 20 wt.%, the HDS conversion of the catalysts shows a declining trend; when the content of zeolite was 40%, the HDS conversion of the catalyst becomes the lowest, only about 60%, and the dropping trend in HDN conversion is more serious than that of HDS.

Table 13
Acidity distribution of supports modified with F

Sample	Acidity (A $cm^2\ g^{-1}$)					
	200 °C			350 °C		
	B	L	B + L	B	L	B + L
Y/CTS	2.7	2.7	5.4	0.3	0.2	0.5
1FY/CTS	4.9	7.1	12.0	0.3	0.7	1.0
2FY/CTS	3.2	9.1	12.3	0.2	0.5	0.7
3FY/CTS	1.6	5.8	7.4	0.2	0.5	0.6
4FY/CTS	1.3	6.5	7.8	0.2	0.4	0.5
5FY/CTS	1.1	6.3	7.4	0.1	0.4	0.5

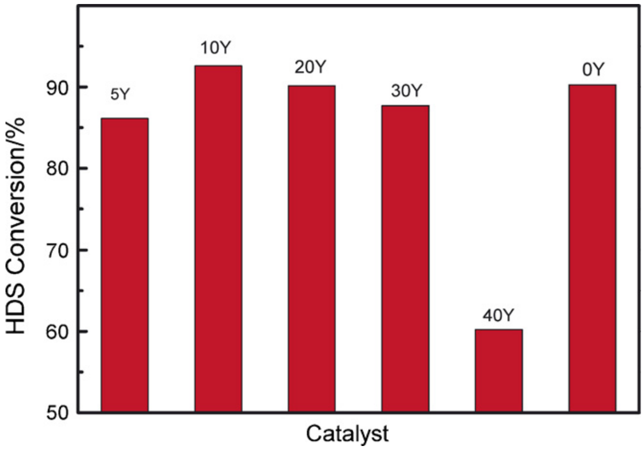

Fig. 8. HDS conversions of the catalysts with various contents of HY.

The sulfur compounds and nitrogen compounds in the CGO are bulky heterocyclic molecules, so large diameter pores are needed for a hydrotreating catalyst. With the increasing content of HY zeolite, the average pore diameter of Y/CTS decreased (shown in Table 3), and the HDS and HDN conversions of the catalyst declined. So, the pore structure of the catalyst obviously affected its HDS and HDN conversions.

The HDS and HDN reactions occurring during CGO hydrotreating process demand different acidities of the catalyst [2]. When the content of HY zeolite in the support was 5 wt.%, the total acidity of support was lower than that of CTS-4; when the content was 10 wt.%, the total acidity of the support was higher than that of CTS-4. Comparing the HDS conversion of the catalysts based on the two supports, it can be found that the catalyst with higher acidity had better HDS conversion, but its HDS conversion was not obviously improved. When the HY content is 20 wt.% or higher, the hydrotreating performance of the catalyst showed a declining trend, the total amount of acidity and proportion of L acidity in the support were more than that of 10Y/CTS, so only improving the acidity of the catalyst cannot improve the hydrotreating performance. The best way to improve the hydrotreating performance of the catalyst was adjusting the B and L acidity to an appropriate proportion.

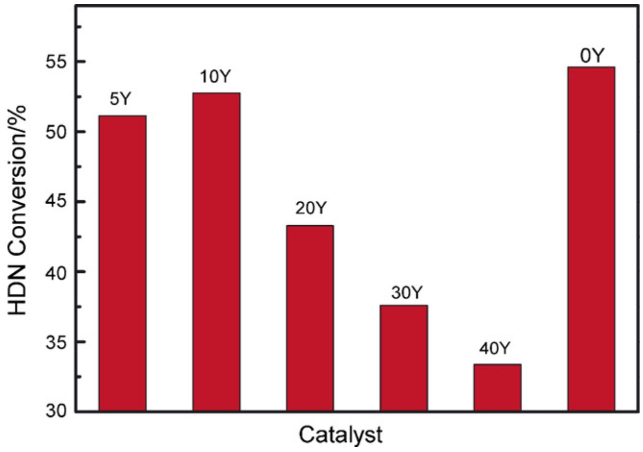

Fig. 9. HDN conversions of the catalysts with various contents of HY.

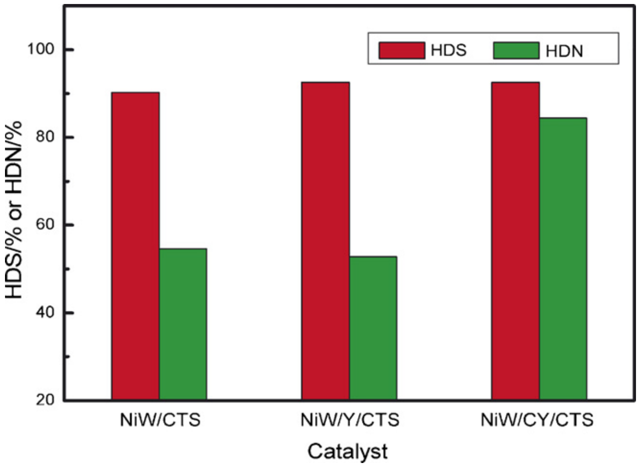

Fig. 10. Hydrotreating performances of NiW/CTS, NiW/Y/CTS and NiW/CY/CTS.

3.6.2. *Influence of HY zeolite pretreatment on the catalytic performance*

Fig. 10 shows the hydrotreating results of NiW/CTS, NiW/Y/CTS and NiW/CY/CTS. It can be seen that the HDS conversions of the three kinds of catalysts are about 85%, but the HDN conversion of NiW/CY/CTS was higher than that of NiW/CTS and NiW/Y/CTS by about 30%. The acidity distribution of CY/CTS was improved by HY zeolite pretreatment comparing with CTS and Y/CTS (shown in Table 10). It can be concluded that the suitable acidity densities and distribution are beneficial to the improvement of the performance of the CGO hydrotreating catalyst.

3.6.3. *Influence of P and F modification on the performance of the catalysts*

P modification of the NiW/10Y/CTS catalyst. Figs. 11 and 12 show the HDS and HDN conversions of the catalysts with various contents of P. From the two figures, it can be drawn that the HDS and HDN conversions rise up at first and then fall down with the increasing addition of P to the support, and the maxima of HDS and HDN conversion were 91.38% and 62.52%, respectively, when the content of P was 3 wt.%. The

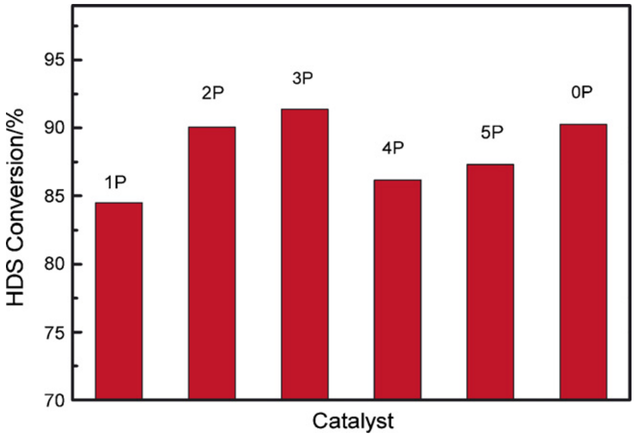

Fig. 11. HDS conversions of the catalysts with various contents of P.

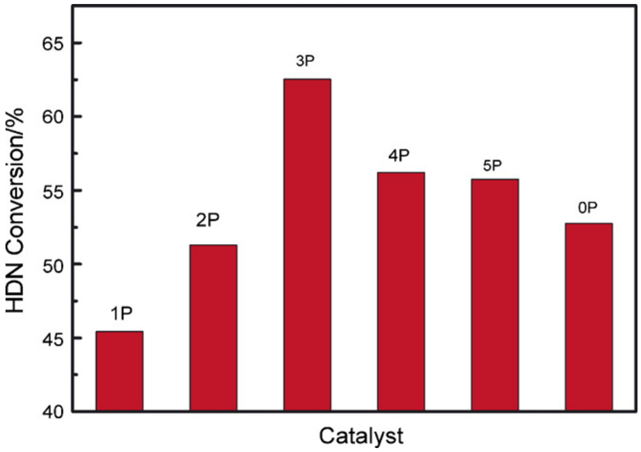

Fig. 12. HDN conversions of the catalysts with various contents of P.

HDS conversion of NiW/3PY/CTS was not much different from that of NiW/Y/CTS, but the HDN conversion of NiW/3PY/CTS was higher by about 10% points than that of NiW/Y/CTS. It is obvious that the addition of P improves the hydrotreating performance of the catalyst and the proper content of P in the support is 3 wt.%. So, we can draw the conclusion that addition of P to the catalyst can improve the catalytic performance of NiW/Y/CTS, and the HDN performance improves more than that of HDS.

F modification of Y/CTS: Figs. 13 and 14 show the HDS and HDN conversions of the catalysts with various contents of F. It can be seen that the HDS conversion of the catalysts increases at first and then falls down with the increasing content of F in the support, and the HDN conversion continuously increases with the increasing content of F. All the HDS conversions of the catalysts prepared with F modified supports are worse than that of NiW/Y/CTS, and the HDN conversions are better than that of NiW/Y/CTS only when the content of F is 5 wt.%.

From the acidity characterization results of P modification on the supports (shown in 11) and the hydrotreating performance results of the resulting catalysts, it can be found that the catalyst hydrotreating performance is not only related to its total acidity amount, but also to the ratio of B to L acidity.

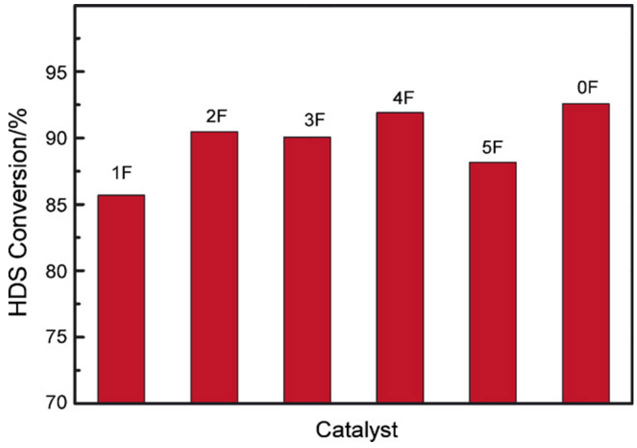

Fig. 13. HDS conversions of the catalysts with various contents of F.

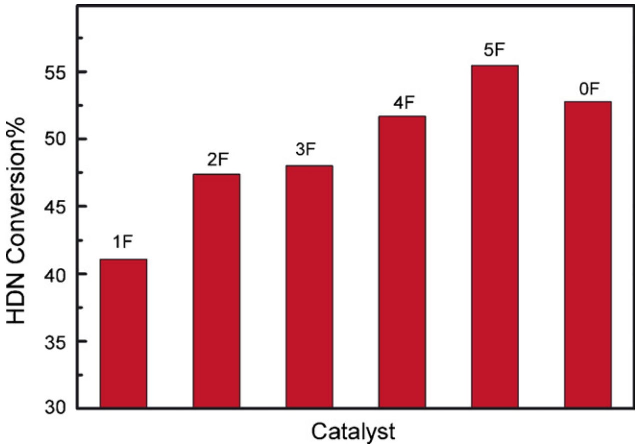

Fig. 14. HDN conversions of the catalysts with various contents of F.

The reason lies in that L acidity improves the hydrogenation of nitrogen-containing heterocyclic compounds, favorable for the improvement of HDN performance. But if there is too much L acidity, the B acidity ratio will become lower correspondingly. And the cracking capability of C–N and C–S bonds decreases, leading to the lower HDS and HDN conversion. If there is too much B acidity, the hydrotreating performance of the catalyst is also depressed although the cracking capability is fine. This is because the lower ratio of L acidity leads to the weak hydrogenation ability. Too much B acidity will also give rise to the poisoning of the catalyst through the incident adsorption of basic nitrogen compounds.

From the acidity characterization results of the F modified supports and the hydrotreating performance results of the catalysts prepared with the modified supports and unmodified ones, it can be found that the total acidity amount in the support and the ratio of L acidity increased when P and F were introduced to the support. The L acidity increased and the B acidity remained unchanged when the support was modified with P, but the B acidity decreased when the support was modified with F. The hydrotreating performance of catalyst reflected the acidity adjustment of the catalyst as it is modified with P and F. That is, the catalysts with proper ratio of B and L acidity work well for both HDS and HDN.

4. Conclusions

CTS-*n* is a series of materials synthesized in the present investigation. This series of materials are featured by their large specific surface area, pore volume and pore diameter and controllable acidity and thus meet the requirements of CGO hydrotreating catalyst support.

This paper proposed and realized the method for CTS-*n* to overgrow on the outer surface of HY zeolite and thereby a novel type of Y/CTS supports was obtained. Y/CTS was featured by the well defined distribution of pore diameter and acidity.

The pore structure and acidity of the Y/CTS can be adjusted by means of Y zeolite dealumination with citric acid and P or/and F modifications. The hydrotreating results of the catalysts indicated that the hydrotreating capability especially HDN conversion could be significantly improved by adjusting the support acidity. The catalysts with proper B acidity and L acidity functioned well in both HDS and HDN. And the catalyst prepared with Y/CTS as support met the requirements of CGO hydrotreating catalyst for pore diameter and acidity.

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