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Preparation of NiW catalysts with alumina and zeolite Y for hydroprocessing of coal tar

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Abstract：γ-alumina supported Ni-W catalysts with different zeolite Y contents were prepared and characterized by N_2 sorption, XRD, H_2-TPR and NH_3-TPD. Their catalytic activities were investigated on a trickle bed reactor by hydroprocessing cresol-naphthalene model compounds in *n*-heptane solution. The results show that all the catalysts exhibit excellent hydrodeoxygenation and hydrogenation activities, while the isomerization and ring-opening products increase with the addition of zeolite, and *trans*-decalin is preferred with acid sites. A better catalyst was selected for hydroprocessing a low temperature coal tar fraction and the product oil was analyzed by GC-MS and elementary analysis. Phenols and *di*-aromatics in the tar are almost converted into indans, cycloalkanes and hydro-aromatics. In the meantime, heteroatoms, especially S and O atoms, reduce remarkably.

Keywords：low temperature coal tar; hydroprocessing; catalyst; zeolite

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Coal tar is the liquid by-product during coal pyrolysis. In a certain extent, coal tar is similar to heavy fractions of petroleum crude and is a potentially abundant feedstock for an oil refinery[1]. However, it is rich in aromatics and heteroatomic compounds in coal tar. Considering this, it needs to be hydrotreated to meet the fuel requirements and the rigorous environmental regulations by simultaneous hydrodearomatization（HDA）, hydrodeoxygenation（HDO）, hydrodenitrogenation（HDN）and hydrodesulfidation（HDS）. Hydrogenation of aromatics in fuel is an effective process to reduce the particulate matters in the exhaust. HDO plays a minor role in petroleum refining process, since the O content in conventional petroleum is less than 2%. But in those feeds derived from low temperature（450 ~ 700 ℃）pyrolysis of coal, especially brown coal, the oxygen content is remarkably higher and even may approach 50%, HDO is rather crucial for their upgrading[2].

Alumina supported Mo（W）-sulfide catalysts with nickel or cobalt as promoters have long been used for the hydroprocessing of petroleum fractions. With the aim to enhance the hydrocracking ability of the catalysts, more acid supports such as zeolite and TiO_2 have also been used[1,3~7]. Besides the conventional cracking function of the acidic sites, the catalytic activities for hydrogenation unsaturated compounds and removal of heteroatoms are also improved with zeolite supports[8~10].

In this work, cresol-naphthalene in *n*-heptane solution was selected as model feed and hydrotreated on NiW/γ-Al_2O_3 catalysts with different zeolite content. The catalytic activities for hydrogenation of naphthalene at the presence of cresol and for hydrodeoxygenation of *p*-cresol were investigated. The most active catalyst was selected for hydroprocessing of a low temperature coal tar fraction.

1   Experimental

1.1   Catalysts preparation

NaY zeolite（SiO_2/Al_2O_3 = 5. 1）was ion exchanged with 1 mol/L NH_3NO_3 at 85 ℃ for 3 h, dried at 120 ℃ for 2 h and calcined at 550 ℃ for 4 h, then the procedure repeated for another time. The mixed supports with different zeolite content were prepared by mixing the zeolite, alumina and a binder, extruding to form cylindrical extrudate, drying at 120 ℃ for 2 h and calcining at 550 ℃ for 4 h.

The catalysts with 4% NiO and 26% WO_3 loading were prepared by incipient wetness method. The grounded 20 ~ 40 mesh mixed supports were co-impregnated with an aqueous mixture of Ni（NO_3）$_2$ · $6H_2O$ and（NH_4）$_6W_7O_{24}$ · $6H_2O$ in appropriate amount at ambient temperature for 3 h, dried at 120 ℃ for 3 h and then calcined at 500 ℃ for 4 h. The catalysts are denoted as AlY*x*, where *x* is the

content of zeolite in the mixed support.

1.2 Catalysts characterization

The BET specific surface area (SSA), pore volume (PV), and average pore diameter (APD) were obtained from N_2 adsorption-desorption isotherms measured at 77 K by a Builder SSA-4300 absorber (Beijing Builder Tech., Ltd.). Before adsorption, the samples were vacuum treated at 373 K overnight. Surface area was calculated with the multipoint BET equation with linear region in the p/p_0 range of 0.05 ~ 0.30.

The X-ray diffraction patterns were obtained with a Rigaku DMAX-RB 12 KW diffractometer using Cu $K\alpha$ radiation, at 40 kV and 150 mA.

H_2-TPR experiments were carried out using a TP-5000II auto-absorber (Tianjin Xianquan Tech., Ltd.) with a TCD detector. About 50 mg of catalyst sample was placed in the center of a quartz tube reactor with quartz wool plugs. Prior to reduction, the samples were pretreated in 30 mL/min N_2 flow to a final temperature of 300 ℃ at 10 ℃/min and held for 30 min, then cooled to ambient temperature. The N_2 was replaced by N_2-H_2 gas mixture with a flowrate of 27 and 3 mL/min, respectively. After the baseline was steady, the temperature of the reactor was increased linearly to 900 ℃ at 10 ℃/min and then retained isothermally for 10 min. The gas was dehydrated by 5A molecular sieve and then detected by a TCD detector at 60 ℃.

NH_3-TPD was performed on Micromeritics Autochem II 2920 absorber. About 40 mg samples were placed in U-tube, heated to 200 ℃ at 40 mL/min N_2 for 30 min, cooled to 100 ℃ and replaced with 15% NH_3 for 30 min. Then 40 mL/min He was purged for another 30 min before the samples were heated to 800 ℃ at 10 ℃/min. The TCD signal of the desorbed gas was recorded.

1.3 Hydroprocessing of model compounds

The hydroprocessing experiments were conducted in a micro scale fixed-bed reactor (12 × 400 mm) operated in down-flow mode. A simplified scheme of this system is shown in Figure 1. To ensure the catalyst bed was maintained at the desired isothermal temperature, the reactor was heated by a three-sector electric furnace. During experiments, the temperature of catalyst bed was monitored closely by a thermocouple located in a thermowell at the center of the reactor.

1 g catalyst was diluted with quartz sand with the same particle size to 9 mL. The mixture was loaded in the middle sector of the reactor with quartz wool plugs below and up the catalyst bed. Prior to each hydrotreating reaction, the catalyst was pre-sulfided in

situ with 5% CS_2-n-heptane solution under the following conditions: drying in H_2 flow at 150 ℃ for 1 h; pressuring up to 4 MPa hydrogen and pumping in the sulfiding feed; elevating the temperature to 230 ℃ at 5 ℃/min and holding for 2 h, then heating to 400 ℃ at 5 ℃/min and keeping for 2 h. During the pre-sulfiding reaction, the LHSV and hydrogen/oil ratio was 2 h^{-1} and 600, respectively.
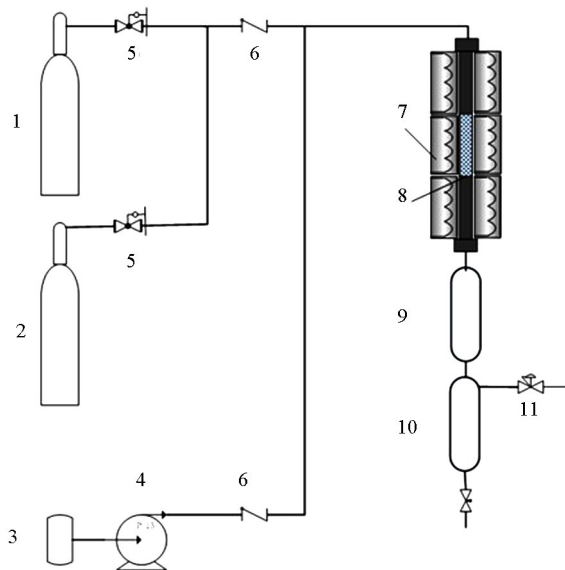

Figure 1　Simplified schematic diagram of the reaction system
1: H_2 cylinder; 2: N_2 cylinder; 3: feed tank;
4: HPLC metering pump; 5: gas regulator; 6: valve;
7: electric furnace; 8: reactor; 9: condenser;
10: gas-liquid separator; 11: back pressure regulator

After the pre-sulfidation, the reactor was cooled to 380 ℃ and the feedstock was introduced. n-heptane solution containing 5% cresol and 4.5% naphthalene was selected as model feed to test the hydrotreating activities of different catalysts. The experiments were carried out at 3 MPa hydrogen pressure, LHSV of 2 h^{-1} and hydrogen/oil ratio of 600.

The liquid products were identified using a GC-MS (Varian 4000) with a methylsilicon capillary column (VF-5ms 60 m×0.25 mm) and the products distributions were quantitatively analyzed by a gas chromatography with a FID detector (Beifen GC3420), employing a diatomite packed column (Apiezon L, 3 m×4 mm).

1.4 Hydroprocessing of coal tar fraction

Two catalysts were selected for hydroprocessing of a real feedstock which was the < 300 ℃ fraction of a low temperature coal tar. 3 g catalyst was diluted with quartz sand to 15 mL and was pre-sulfided with the same LHSV and gas/oil ratio as above. The

hydroprocessing reaction was performed under 8 MPa at 380 ℃ with LHSV of 1 h^{-1} and H$_2$/oil of 1 000. The product from the 2*nd* to the 5*th* hour was collected for analysis.

The contents of C, H, N and O in the oil were analyzed on Elementar Vario MICRO cube analyzer (Elementar Analysen Systeme, Germany). S was determined by monochromatic wavelength dispersive X-ray fluorescence spectrometry according to ASTM D7039.

The compositions of the liquids were analyzed by GC-MS (VARIAN 4000, US), and then quantitatively analyzed by the total ion chromatogram (TIC spectrum) with simple area normalization method.

2　Results and discussion
2.1　Characterization of catalysts

The texture data of the catalysts with different zeolite content are given in Table 1. The SSA, PV and APD of the catalysts decrease with the addition of zeolite content, except that AlY10 mainly due to the pressure control during the extrusion (manual operation). With the increase of zeolite, the micropores of the catalysts increase, while the mesopores and macropores decrease.

Table 1　Texture properties of the catalysts

Catalyst	SSA $A/(m^2 \cdot g^{-1})$	PV $/(mL \cdot g^{-1})$	APD d/nm	Pore size distribution /%		
				micropore	mesopore	macropore
AlY0	86.28	0.34	15.82	3.1	93.1	4.8
AlY3	78.65	0.28	14.02	5.3	92.7	2.2
AlY5	73.93	0.20	11.08	8.6	91.1	0.3
AlY10	66.58	0.26	15.86	2.5	90.8	6.7

Figure 2 presents the XRD traces of the samples. The XRD patterns of all the catalysts exhibited only broad XRD peaks of γ-alumina, even though the strength were reduced sharply, while no additional peaks belonging to crystalline Ni and W compounds were observed. This means that supported Ni and W species are highly dispersed on the support surface, either completely amorphous or composed of crystallites smaller than 4 nm which is under the detect limit of this XRD device. The peaks of zeolite Y in the small angle zone (< 30°) were more obvious with the increase of zeolite content in the mixed supports.
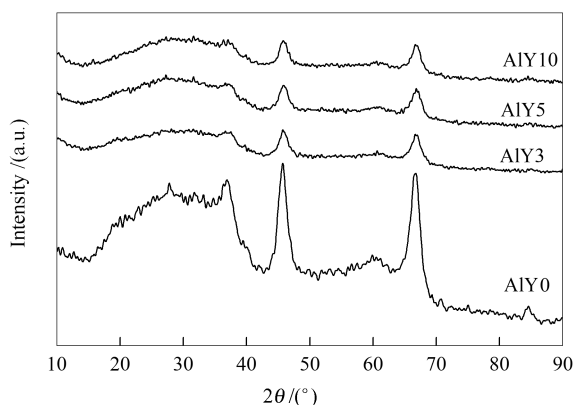
different temperatures. With the increase of zeolite content, the peaks especially the one at 750 ℃, mainly due to the reduction of W species, become weaker. It indicates that metal oxides on the catalyst surface is more difficult to be reduced since the metal-support interaction is modified with the addition of zeolite Y. Inamura et al[11] also observed the different reducibility of the metal precursor on the supports with different zeolite content. Breysse et al[12, 13] pointed out that by affecting the interaction between the active phase precursor and the support, the acidity change the electronic properties of the metal and thus modify the properties of the catalysts.
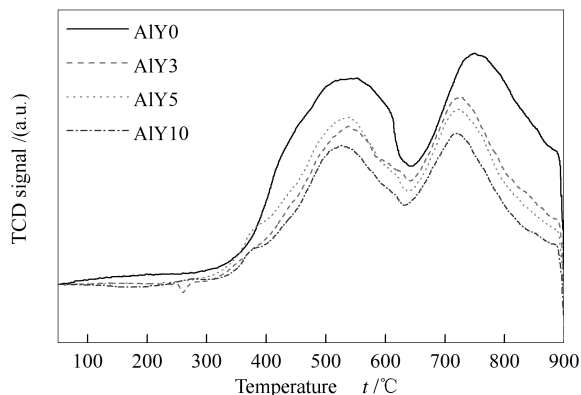

Figure 2　XRD profiles of the catalysts and support

Figure 3　H$_2$-TPR curves of the catalysts with different zeolite

Figure 3 shows the H$_2$-TPR profiles of the catalysts. The TCD signal shows hydrogen consumption with reduction of metal oxides at

The acidity of the catalysts measured by NH$_3$-TPD (Figure 4) shows that the acidic sites on the catalysts surface increase with the addition of zeolite

Y. The desorption profiles show that the relative strengths of the acidity sites are almost the same. The peak temperatures are about 300 ℃, which indicated that weak acids are predominated on the catalysts surfaces.
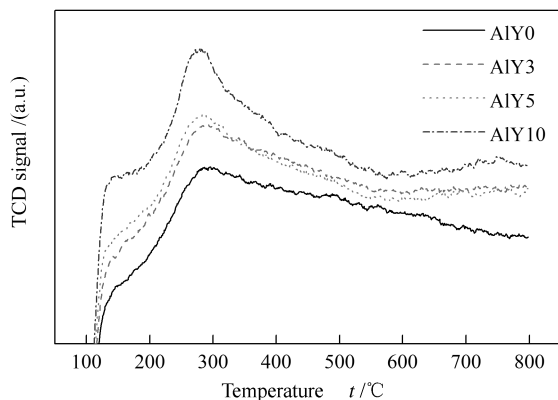

Figure 4　NH₃-TPD profiles of different catalysts

2.2　Catalytic activity

The catalytic activity was evaluated by hydroprocessing of cresol-naphthalene mixture in *n*-heptane solution. The products identified by GC-MS consist mainly of methylcyclohexane, toluene, tetralin, *trans*- and *cis*-decalin, naphthalene; with zeolite catalysts, methylindan, butylbenzene and a little methyltetralin, methylnaphthalene, xylene, ethylcyclopentane and indan are also detected. The product distribution measured by GC-FID is shown in Table 2.

Cresol is negligible in all cases under such conditions. Methylcyclohexane is the main component (by differential) and the yield of toluene is the second among the cresol HDO product in all cases. Wandas et al[14] concluded that the reaction pathway of ring saturation followed by oxygen removal (by direct dehydration) predominates with $CoMo/Al_2O_3$ catalysts during cresol hydrodeoxygenation. It seems that the same conclusion can be made with these NiW catalysts used in the experiments. Moreau et al[15,16] suggested that if the direct HDO reaction was predominant, toluene would have to be the main product since hydrogenation of monocyclic aromatics to corresponding cyclohexanes proceeds with difficulty. The yields of toluene decrease with the increase of zeolite content in the catalysts, which indicates that the saturation-deoxygenation pathway is more preferred with more acidic sites during the hydrotreating of cresol. No evident intermediates such as methylcyclohexanol are observed in the products, which suggests that dehydration of these compounds would be very fast in comparison with the reaction of ring hydrogenation.

Table 2　Catalysts performance in hydroprocessing of naphthalene and cresol

Catalyst	Cresol conv. x /%	Naph. conv. x /%	Yield w/%			*trans-/cis-* DeHN
			toluene	DeHN	TeHN	
AlY0	99.80	77.75	35.99	10.30	61.26	4.2
AlY3	98.97	79.91	29.38	8.48	45.68	5.2
AlY5	98.59	85.41	22.67	9.63	40.45	6.0
AlY10	98.34	86.03	20.26	9.99	33.98	5.9

reaction conditions: p_{H_2} = 3 MPa, t = 380 ℃, LHSV = 2 h⁻¹, H₂/oil = 600(volume ratio), 1 g catalyst

Naphthalene is hydrogenated to *trans*- and *cis*-decalin via a partially hydrogenated intermediate tetralin. By inhibiting the condensation of alkyl radicals, decalin and tetralin could help improve the thermal stability of alkanes as hydrogen donors[17]. With the addition of zeolite, the conversion of naphthalene increases. Though the yield of decalin increases slightly, the one of tetralin reduces sharply. Carboncations-involved reactions have long been proposed as the main hydrotreating mechanism. The influence of the support acidity on the hydrogenation and cracking functionality of the hydrotreating catalyst were both attributed to the presence of Brönsted acid sites. But it seems the later one is affected more significantly with these zeolite containing catalysts. In the other hand, this demonstrates that the active metal sites are relatively less than the acidity sites, or the distances between the two kinds are not short enough for the transference of active hydrogen atoms to unsaturated species, which induce that the hydrogenation ability is weaker than the cracking ability. The decrease of the metal reducibility with the addition of zeolite may also account for this imbalance.

The *trans-/cis*- DeHN ratio increases with the addition of zeolite to different extent. The improvement with AlY series is more significant, mainly because the differences between the acidity of AlY catalysts are more evident. It seems that acidity favors the production of *trans*-DeHN, either directly or by promoting the isomerization of *cis*-DeHN to DeHN. Schmitz et al[18] also concluded that the

*trans-/cis-*DeHN ratio increases with acidic site density during the hydrogenation of naphthalene with Pt(Pd)/zeolite catalysts.

Other hydrocarbons such as ethylcyclopentane, xylene, butylbenzene, methylindan, methyltetralin and methylnahthalene formed by isomerization, carbon chain rearrangement or methylation are also detected. Ethylcyclopentane and methylindan are isomerized from methylcyclohexane and tetralin, respectively, while butylbenzene is a ring-opening product of the later. As to the methylation of toluene and tetralin to xylene and methyltetralin, Wandas et al[14] concluded that the aromatic ring with delocalized

π-bond tend to be attacked by active electrophile such as $+CH_3$ formed with $\cdot CH_3$ at acid sites. Such kinds of reactions are all involved carboncations which are favored with Brönsted acids in zeolite Y. This can explain why with the addition of zeolite in the catalysts the conversion of naphthalene increases, while the total amount of tetralin and decalin decrease.

Based on the results above, the reaction pathways for naphthalene hydrogenation and *p*-cresol hydrodeoxygenation on these catalysts with different zeolite contents are put forward in Figure 5.
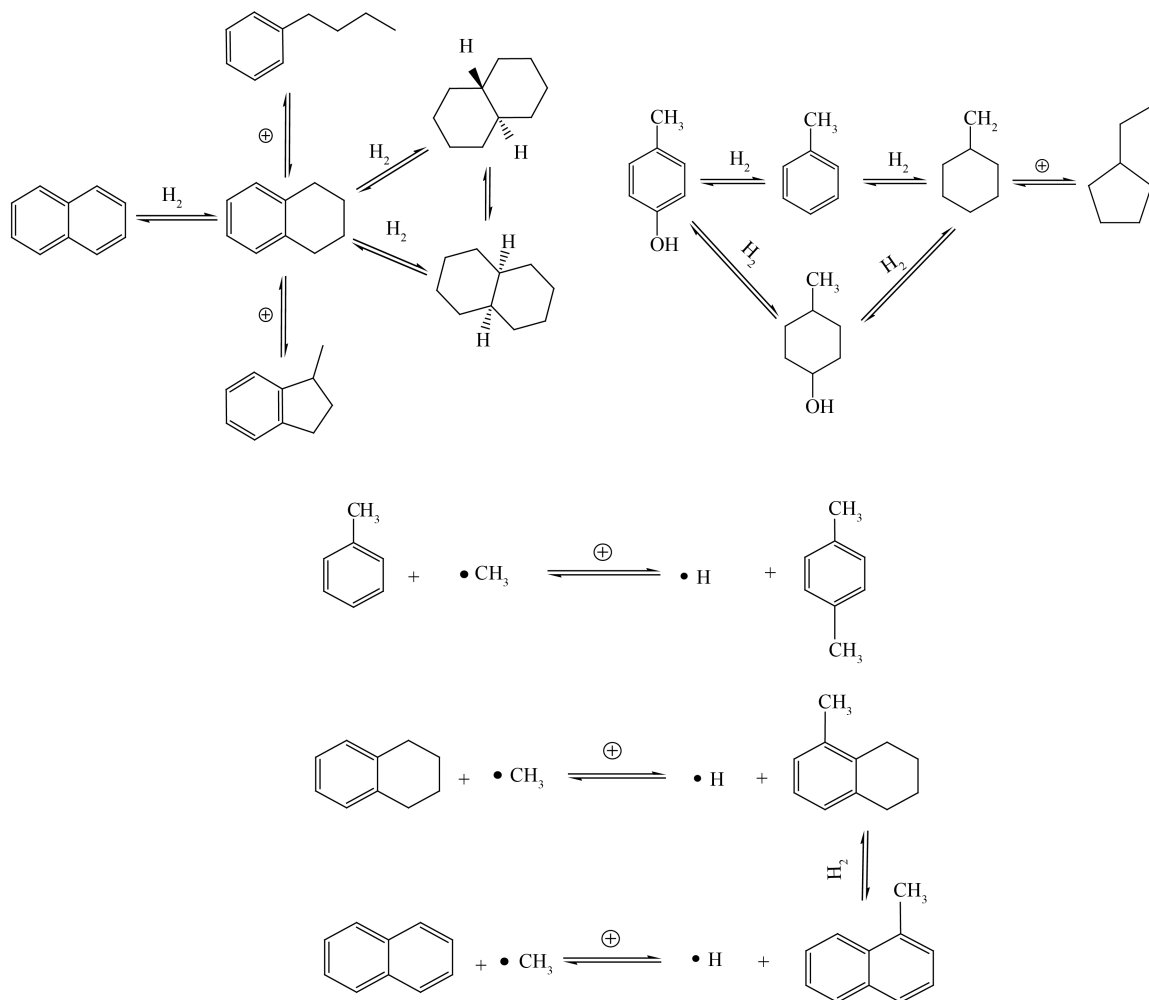

Figure 5   Reaction pathways for naphthalene hydrogenation and *p*-cresol hydrodeoxygenation
reaction conditions：$p_{H_2} = 3$ MPa, $t = 380$ ℃, LHSV = 2 h^{-1}, H$_2$/oil = 600(volume ratio), 1 g catalyst

2.3 Hydroprocessing of coal tar

AlY5 was selected for hydrotreating of the < 300℃ fraction of a low temperature coal tar. The elementary composition of the feed and the hydrotreated product are shown in Table 3. After

being hydroprocessed with AlY5, the H/C atomic ratio raises from 1.09 to 1.51, mainly due to the addition of hydrogen and the elimination of heteroatoms, particularly O atoms. The HDN, HDS and HDO activities of AlY5 are 38.1%, 89.2% and

77. 9%, respectively. Compared to the product on AlY0 without zeolite, the S and O content in the one on AlY5 are much lower, while the H/C atomic ratio is higher.

Table 3   Elementary composition of the oil before and after hydroprocessing

	Ultimate analysis $w/\%$				$S /(mg \cdot kg^{-1})$	H/C(atomic ratio)
	C	H	N	O		
Feed	80. 28	7. 29	0. 46	1600	10. 70	1. 09
AlY0	83. 94	9. 97	0. 29	200	3. 43	1. 43
AlY5	79. 74	10. 03	0. 29	173	2. 47	1. 51

reaction conditions: p_{H_2} = 8 MPa, t = 380 ℃, LHSV = 1 h^{-1}, H_2/oil = 1 000(volume ratio), 3 g catalyst

The distillate distribution of the feed and its hydrotreated product are shown in Figure 6. After hydroprocessing, the fractions below 130 ℃ increase by 12. 1% compared with the feed oil whose IBP is 186 ℃. Without secondary cracking during the pyrolysis process, low temperature coal tar has less light fraction and its IBP is generally higher than the one from coke oven. The jet fuel fractions between 130 and 280 ℃ decrease from 83. 5% to 68. 3%, mainly due to the elimination of O atoms in phenolic compounds to form lighter hydrocarbons.
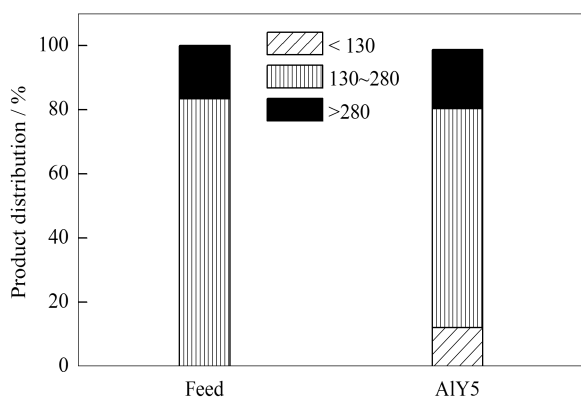

Figure 6   Product distribution of
the hydroprocessed coal tar fraction
reaction conditions: p_{H_2} = 8 MPa, t = 380 ℃,
LHSV = 1 h^{-1}, H_2/oil = 1 000(volume ratio), 3 g catalyst

The compositions of the feed and its hydrotreated products analyzed by GC-MS are shown in Figure 7. Phenols and 2-ring aromatics are the main components in the feed; after hydroprocessing, the content of 1-ring aromatics, indans, cycloalkanes and hydro-aromatics such as tetralin and decalin increase significantly in the liquid product.

The aromatics, olefins and saturates in 130 ~ 280 ℃ fraction of the hydrotreated product were determined by FIA method. The contents of saturates, aromatics and olefins with AlY5 are 43. 2%, 52. 9% and 3. 9%, respectively. Since the feed consists mainly of phenols and *di*-aromatics, especially phenols, the sample is too dark with strong polarity to analyze with this method. However, from the blur boundary of the desorption it can be seen that the saturates are of a little. This indicates that most of the saturates in the products is obtained by hydroprocessing. One thing should be aware that since olefins are more active than other unsaturated hydrocarbons, the olefins here during the test may be referred to part of the hydroaromatics.
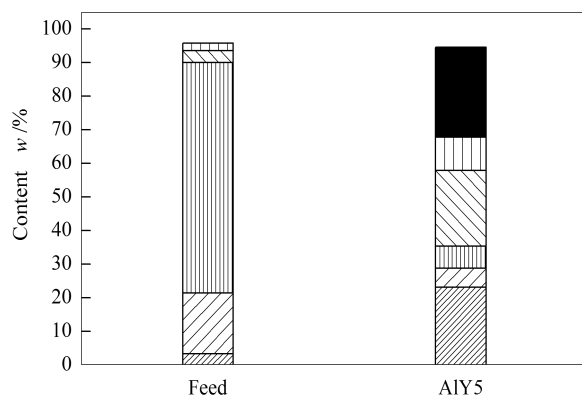

Figure 7   Composition of the coal
tar before and after hydroprocessing
▨: 1-ring aromatics; ▧: 2-ring aromatics;
▥: phenol; ◇: indenes; ▭: aliphatic;
■: cycloalkanes & hydro-aromatics
reaction conditions: p_{H_2} = 8 MPa, t = 380 ℃,
LHSV = 1 h^{-1}, H_2/oil = 1 000(volume ratio), 3 g catalyst

3   Conclusions

Hydrotreating of cresol-naphthalene in *n*-heptane solution was investigated using a series of NiW/ Al_2O_3-Y catalysts with different zeolite content. Cresol is almost converted in all cases. The saturation-deoxygenation pathway is more preferred with more acidic sites. Naphthalene is converted to decalin via tetralin. With the addition of zeolite in the catalysts, more and more ring-opening and isomerization products such as butylbenzene and methylindan are detected, and *trans*-decalin is preferred with acid sites. Hydroprocessing of the < 300 ℃ fraction from a low temperature coal tar with AlY5 significantly reduces the content of phenol and

2-ring aromatics，while their hydrotreating products such as indan，cycloalkanes and hydroaromatics with higher volumetric heat value and thermal stability，increase sharply. The heteroatoms，especially S and O atoms，reduce remarkably.

Acknowledgement

References

［1］ SAYAN S, PAUL J. Hydrogenation of naphthalene and methylnaphthalene：modeling and spectroscopy［J］. J Mol Catal A：Chem, 2002, **185**(1/2)：211-222.

［2］ FURIMSKY E. Catalytic hydrodeoxygenation［J］. Appl Catal A：Gen, 2000, **199**(2)：147-190.

［3］ RAM REZ J, RAYO P, GUTI RREZ-ALEJANDRE A, ANCHEYTA J, RANA M S. Analysis of the hydrotreatment of Maya heavy crude with NiMo catalysts supported on TiO₂-Al₂O₃ binary oxides：Effect of the incorporation method of Ti［J］. Catal Today, 2005, **109**(1/4)：54-60.

［4］ WANG L, SHEN B, FANG F, WANG F, TIAN R, ZHANG Z, CUI L. Upgrading of light cycle oil via coupled hydrogenation and ring-opening over NiW/Al₂O₃-USY catalysts［J］. Catal Today, 2010, **158**(3/4)：343-347.

［5］ ARRIBAS M A, MARTÍNEZ A. The influence of zeolite acidity for the coupled hydrogenation and ring opening of 1-methylnaphthalene on Pt/USY catalysts［J］. Appl Catal A：Gen, 2002, **230**(1/2)：203-217.

［6］ LEITE L, BENAZZI E, MARCHAL-GEORGE N. Hydrocracking of phenanthrene over bifunctional Pt catalysts［J］. Catal Today, 2001, **65**(2/4)：241-247.

［7］ HASSAN A, AHMED S, ALI M A, HAMID H, INUI T. A comparison between ［beta］- and USY-zeolite-based hydrocracking catalysts［J］. Appl Catal A：Gen, 2001, **220**(1/2)：59-68.

［8］ GALLEZOT P. The state and catalytic properties of platinum and palladium in faujasite-type zeolites［J］. Cat Re-Sci Eng, 1979, **20**(1)：121-154.

［9］ ZHENG J, GUO M, SONG C. Characterization of Pd catalysts supported on USY zeolites with different SiO₂/Al₂O₃ ratios for the hydrogenation of naphthalene in the presence of benzothiophene［J］. Fuel Process Technol, 2008, **89**(4)：467-474.

［10］ YASUDA H, SATO T, YOSHIMURA Y. Influence of the acidity of USY zeolite on the sulfur tolerance of Pd-Pt catalysts for aromatic hydrogenation［J］. Catal Today, 1999, **50**(1)：63-71.

［11］ INAMURA K, IINO A. Development of zeolite hydrocracking catalyst and system for resid hydrodesulfurization unit［J］. Catal Today, 2011, **164**(1)：204-208.

［12］ BREYSSE M, CATTENOT M, KOUGIONAS V, LAVALLEY J C, MAUGE F, PORTEFAIX J L, ZOTIN J L. Hydrogenation properties of ruthenium sulfide clusters in acidic zeolites［J］. J Catal, 1997, **168**(2)：143-153.

［13］ SIMON L J, VAN OMMEN J G, JENTYS A, LERCHER J A. Sulfur-tolerant Pt-supported zeolite catalysts for benzene hydrogenation：I. Influence of the support［J］. J Catal, 2001, **201**(1)：60-69.

［14］ WANDAS R, SURYGALA J, SLIWKA E. Conversion of cresols and naphthalene in the hydroprocessing of three-component model mixtures simulating fast pyrolysis tars［J］. Fuel, 1996, **75**(6)：687-694.

［15］ MOREAU C, AUBERT C, DURAND R, ZMIMITA N, GENESTE P. Structure-activity relationships in hydroprocessing of aromatic and heteroaromatic model compounds over sulphided NiO-MoO₃/γ-Al₂O₃ and NiO-WO₃/γ-Al₂O₃ catalysts：chemical evidence for the existence of two types of catalytic sites［J］. Catal Today, 1988, **4**(1)：117-131.

［16］ MOREAU C, JOFFRE J, SAENZ C, GENESTE P. Hydroprocessing of substituted benzenes over a sulfided CoO-MoO₃/γ-Al₂O₃ catalyst［J］. J Catal, 1990, **122**(2)：448-451.

［17］ SONG C, ESER S, SCHOBERT H H, HATCHER P G. Pyrolytic degradation studies of a coal-derived and a petroleum-derived aviation jet fuel［J］. Energy Fuels, 1993, **7**(2)：234-243.

［18］ SCHMITZ A D, BOWERS G, SONG C. Shape-selective hydrogenation of naphthalene over zeolite-supported Pt and Pd catalysts［J］. Catal Today, 1996, **31**(1/2)：45-56.

NiW/Al₂O₃-Y 催化剂的制备及其对煤焦油加氢处理的研究

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摘　要：以不同比例的 γ-Al₂O₃ 和 Y 型分子筛为混合载体制备 NiW/Al₂O₃-Y 催化剂，采用 N₂ 低温吸附、XRD、H₂-TPR 和 NH₃-TPD 对其进行表征，并在固定床上通过甲酚–萘溶液的加氢处理反应对催化剂活性进行评价。结果表明，催化剂均具有良好的加氢脱氧及加氢饱和性能，异构化及裂化产物随分子筛含量的增加而增加，催化剂酸性增加更有利于萘加氢产物中反式十氢萘的生成。以较佳催化剂对低温煤焦油馏分进行加氢处理，采用 GC-MS 和元素分析等对油品进行分析。原料中绝大部分酚类化合物及双环芳烃转化为茚、环烷烃和氢化芳烃等化合物，同时明显降低了杂原子尤其是硫和氧的含量。

关键词：低温煤焦油；加氢处理；催化剂；分子筛

中图分类号：TQ519 　　　**文献标识码**：A