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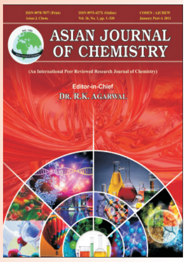

Tailoring Pore Shapes of Catalysts for Diesel Hydrodesulphurization†

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In order to remove macromolecular sulfides with strong steric effects, a new type of alumina support was developed. The pore structures of the alumina supports were optimized by adjusting the aging time, pH levels and peptizing agent during the synthesis process and the extrusion. For study the influence of the new supports on the hydrodesulphurization catalytic property, the pore structure and acidity of the supports were analyzed. The difference of the acidity distribution was characterized by the NH_3-temperature programmed desorption and pyridine-temperature programmed desorption. The acidity levels of NH_3-temperature programmed desorption didn't show obvious change. While the acidity levels of pyridine-temperature programmed desorption of the new support containing clearer pores was higher than that of the conventional supports. This result indicated the new supports favored the absorption of large molecules. Furthermore, the newly catalysts showed a higher desulphurization degree, which led to higher activity.

Keywords: Unblocked pore, Macromolecular sulfides, Desulphurization degree, Ultra-deep HDS, Catalytic activity.

INTRODUCTION

With increasingly rigorous environmental legislations on fuel products, the restrictions on the sulphur content in gasoline and diesel are even more stringent. Europe and other developed regions have implemented strict emission standards which limit the sulphur content in fuel to less than 10 mg/g. The impendent challenges for Chinese refineries include ways to produce clean diesel that can adequately meet the demand of the China IV standard, (which is equivalent to the Euro IV standard), with considerable improvements in high space velocity and meanwhile limiting the revamping costs on existing refineries.

Ultra low sulphur diesel (ULSD), which is different than normal HDS, has a purpose to overcome the steric effect[1-6] of dimethyl-substituted sulfides such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), which puts higher requirements on the support pore structures and acidity of the original supports. The existing catalysts have a shortage of small pores when they are used to remove large molecular sulfides. Therefore, the pore size needs to be amplified to adequately remove macromolecular sulfides such as 4,6-DMDBT and at the same time, improve the acidity and increase the number of active sites of supports[7-12]. Usually, two approaches are considered to achieve alumina supports that have an effective pore size distribution sufficient for adsorption and removal of sulfides. One way to accomplish this is by raising the calcinating temperature of the supports in order to enlarge their pore size. Another way is by adding a macromolecular pore-expanding agent. For example, the alumina supports with large pore sizes can be obtained by the introduction of carbon black during the support shaping process, followed by calcination at high temperature. Although increasing the calcination temperature of supports can potentially increase its pore size, the specific surface area and acidity of the alumina supports are greatly decreased. For the supports that added a macromolecular pore-expanding agent such as carbon black, the packing density, specific surface area and the acidity of the supports decreased greatly reduced after being calcinated at high temperatures. However, due to their enlarged pore sizes, they still do not meet the standard for catalytic activity. In order to obtain the alumina supports with pore structures suitable for the removal of macromolecular sulfides, the pseudoboehmite, which has been prepared by increasing the aging time and pH value, is then combined with a mild acidic peptizing agent that will have little negative influence on supporting the pore structure during its forming process. By utilizing the techniques mentioned above, new alumina supports with high porosity are fabricated with high pore volume, high specific surface area and large pore sizes.

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The results of the catalytic activity testing showed the newly developed catalysts that were based on the highly porous supports exhibit excellent catalytic performance for ultra-deep HDS for treating blended oil of heavy straight-run diesel. The reaction temperature was 10 ºC lower than the same catalysts in the reference samples. In order to study the influence of the new alumina supports on the HDS catalytic property, the pore structure and acidity of the supports were analyzed. NH_3 and pyridine were used as adsorbate because of the obvious difference in their molecular diameters. The difference of acid distribution between the new supports and the conventional ones was characterized by NH_3-temperature programmed desorption (NH_3-TPD) and pyridine-TPD. After presulfiding the catalysts prepared with the two supports, the content of the sulphur in the catalysts was analyzed and the sulphurization degree of the catalysts was obtained. This was helpful in understanding the essence of catalytic activity upgrading.

EXPERIMENTAL

Preparation of support materials and the catalysts: Support S1 used pseudoboehmite (PB) powder as the aluminum source and it was synthesized using aluminum sulfate and sodium aluminate, with citric acid and Sesbania powder as the extrusion assistant and diluted nitric acid as the peptizing agent. By kneading, grinding and extruding it into trilobal supports and performing calcination at 600 ºC, the final sample was obtained. Support S2 was prepared by the same method as S1 except the calcination temperature was performed at 750 ºC. Support S3 chose a pseudoboehmite with a higher pH level and a prolonged aging time during its synthesizing process and then citric acid and Sesbania powder were added as extrusion agents and acetic acid of mild acidity and deionized water was blended for the peptizator. By kneading, grinding and extruding the product into trilobal supports and performing calcination at 600 ºC, the S3 sample was obtained.

Supports S1, S2 and S3 were used for preparing the C1, C2 and C3 catalysts in the same methods, respectively. The catalysts were analyzed after a presulfiding treatment in a 10 mL HDS microreactor and the differences of the sulphur contents between the catalysts were observed to contrast the degrees of sulfidation.

During the preparation of the catalysts, the Mo-Co active metal solution was readied from ammonium heptamolybdate and cobalt nitrate. Using the saturation impregnation method to load the active metal and then drying and calcinating at 200 ºC, the catalysts were ready. The metal contents of MoO_3 and CoO on the catalysts were 22.1 and 3.52 %, respectively.

Evaluation of catalytic performance: In order to investigate the differences on the removal of the macromolecular sulfides of the catalysts using S3 and S1 as supports, the activity was tested on 200 mL HDS pilot-plant and the reactor was filled with 100 mL catalysts mixed with 100 mL quartz sand. The presulphurization of the catalysts was started after a 6.4 MPa pneumatic test. The sulfiding oil was kerosene with an added 2 % CS_2. The reactor was heated from room temperature to 230 ºC at a speed of 30 ºC/h and maintained for 6 h, then the inlet temperature of the reactor was increased to 320 ºC at a speed of 30 ºC/h and maintained for 8 h. After that, the sulphurization was complete. When the sulphurization was finished, stop sulfiding oil and carry out straight-run diesel for 24 h initial activity stability. Then the feedstock was changed out for heavy straight-run diesel, which is used to study the removal activity of macromolecular sulfides. The properties of the feedstock are shown in Table-1. The sulphur contents in the catalysts and oil products were determined by the sulphur contents analyzer ANTEK-9000. The carrier gas was Ar, the burning gas was O_2 and the burning temperature was 1100 ºC. The nitrogen contents of the products were determined by the nitrogen contents analyzer ANTEK-7000. The carrier gas was Ar, the burning gas was O_2 and the burning temperature was 1050 ºC. The content of 4,6-DMDBT sulfide was made with a gas chromatography-atomic emission detector (GC-AED) and a gas chromatography instrument (Agilent 6890 N), atomic emission detectors (HP G2350A), separation column (PONA), with He as the carrier.

TABLE-1
PROPERTIES OF TESTING FEEDSTOCK

Feedstock		Heavy straight-run diesel
Density (20 ºC) (g cm^{-3})		0.8533
Distillation (ASTM-D86) (ºC)	IBP/10 %	217/277
	30 %/50 %	296/309
	70 %/90 %	327/356
	95 %/FBP	369/375
Sulfur (μg g^{-1})		17750
Nitrogen (μg g^{-1})		140
Total aromatics (%)		28.1
PHAS (%)		11.3
4,6-DMDBT (μg g^{-1})		266

Characterization of the materials: In order to study the effects of the support pore structures on the catalyst's performance, the low temperature nitrogen adsorption-desorption method was used. The low temperature nitrogen adsorption-desorption method (BET method) was performed using the physical adsorption instrument model ASAP2400 made by USA MIC Company. Before testing, samples were vacuumized for more than 4 h in 300 ºC. The differences of the acidity distribution between the S3 supports and S1 supports were characterized by temperature programmed desorption (TPD). Ammonia and pyridine were used as adsorbates during the TPD process due to the differences of their molecular diameters. In order to analysis the surface properties of the alumina support, NH_3-TPD was carried out on a DuPont 9900 TG51 thermogravimetric (TG) instrument. The samples were heated to 500 ºC in N_2 for 0.5 h and then cooled down to 150 ºC. After the NH_3 adsorption for 0.5 h, the NH_3 chemical temperature programmed desorption was started at 10 ºC/min until the samples' weights were constant. Moreover, the pyridine-TPD analysis instrument used for testing was an infrared spectrometer model 560 made by Thermo Nicolet Corporation. The samples were purified for 4 h at 500 ºC and 6.0 MPa. The sulphur contents in the catalysts were also analysis by an ANTEK-9000 sulphur analyzer.

RESULTS AND DISCUSSION

Using the C1 catalyst as a reference sample and heavy straight-run diesel as a feed, compared the performance of the three catalysts, the operating conditions and test results are shown in Table-2. It can be seen in Table-2 that the HDS, HDN and aromatics saturation activity of the C3 catalyst was stronger than that of the C1 catalyst. The C_3 catalyst has an especially competitive advantage on the removal of macromolecular sulfides with substituent steric effects such as 4,6-DMDBT. When treating heavy straight-run diesel, the reaction temperature is 10 ºC lower than the C1 catalysts.

TABLE-2
PERFORMANCE OF THREE CATALYSTS FOR TREATING HEAVY STRAIGHT-RUN DIESEL

Catalysts	C3 Catalyst	C2 Catalyst	C1 Catalyst
H_2 pressure (Mpa)	6.0	6.0	6.0
LHSV (h^{-1})	1.5	1.5	1.5
H_2 to oil ratio (V/V)	300	300	300
Reaction temp. (ºC)	360	360	370
Refined oil properties			
Density@ 20 ºC (g/cm^3)	0.8235	0.8249	0.8242
Distillation range (ºC) (ASTM-D86)	144-372	146-374	140-373
IBP/10 %	144/243	146/258	140/256
30 %/50 %	277/296	282/300	280/299
70 %/90 %	314/347	317/349	316/348
95 %/FBP	367/372	368/374	368/373
Sulfur (μg g^{-1})	7.0	30.6	8.0
Nitrogen (μg g^{-1})	1.0	3.6	1.5
Aromatics (%)	13.1	15.8	15.0
PHAS (%)	1.9	3.2	2.4
4,6-DMDBT (μg g^{-1})	3.2	15.9	4.3

The N_2 adsorption-desorption curve of original support S1 and new support S3 are shown in Fig. 1. Fig. 1 showed that the adsorption quantity of S3 and its gradient of the N_2 adsorption-desorption curve are higher than those of S1. However, the distance range of the hysteresis loop in the adsorption-desorption curve of S3 was shorter than that of S1 (relative pressures of S1 and S3 were 0.4-1.0 and 0.5-1.0, respectively). This indicates that compared to S1, the pores of support S3 are more open, which is beneficial to the adsorption-desorption of large molecules. In other words, the pore structures of S3 are unobstructed and favorable to the adsorption-desorption of macromolecular sulfides, which can improve the number of active sites and the intrinsic activity. Fig. 2 showed that the pore diameter of support S3 increases and the pore size distribution is more concentrated than that of support S1, which is also advantageous to the adsorption-desorption of macromolecular sulfides.

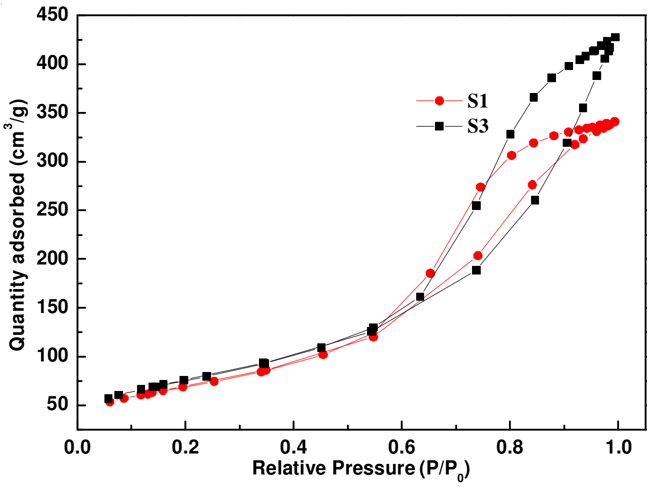

Fig. 1. N_2 adsorption-desorption curves of supports S1 and S3

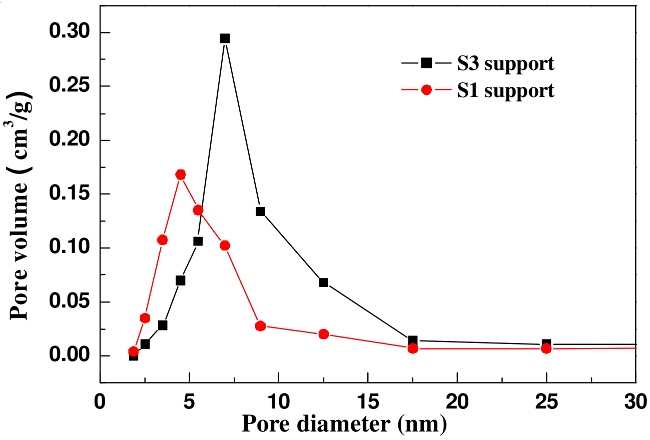

Fig. 2. Pore size distribution curves of supports S1 and S3

TABLE-3
PROPERTIES OF DIFFERENT SUPPORTS

Supports	S1	S2	S3
Preparation method	Normal	Carbon black added	New method
Pore volume (mL g^{-1})	0.59	0.70	0.71
Specific surface area (m^2 g^{-1})	371	302	371
Average pore size (nm)	6.4	9.3	7.7
Bulk density (g cm^{-3})	0.60	0.47	0.55
Strength (N cm^{-1})	132	86	128

The properties of the pore structures, bulk densities and strengths of supports S1, S2 and S3 are shown in Table-3. In Table-3, it can be seen that adding carbon black increased the pore sizes of the prepared supports. At the same time, the bulk density, specific surface area and strength of the supports all decreased dramatically. The decreasing of the support's strength can potentially influence the applied performance of the catalysts; meanwhile, the support acidity can be decreased after calcinating at 750 ºC which decreases the number of active sites. The support S3 was prepared by increasing the crystallization time and pH level during the synthesizing of the pseudoboehmite. A mild acid was used as a peptizing agent and had little negative effect on supporting the pore structures during its forming process. Compared to S1, the pore sizes and volumes of S3 were superior, but the specific surface area was almost the same. Even though the decreased range of the bulk density of S3 was lower than that of S2 and there was a slight decrease of the support strength, S3 was still able to meet the application requirements of commercial catalysts. Therefore, compared to S1 and S2, S3 would be more suitable for catalyst supports of diesel ultra-deep HDS.

The "surface acidity site" for alumina represents the hydroxyl number, which coordinates with the unsaturated aluminum atom on the surface of the alumina. More acidity sites on the surface mean more active sites on the catalysts. The surface of alumina has three types of aluminum atoms with different coordinations *i.e.*, high coordination of aluminum atoms (low surface energy), moderate coordination of aluminum atoms (moderate surface energy) and low coordination aluminum atoms (high surface energy). Accordingly, there are three types of hydroxyl groups, which indicate different acidity sites for adsorption stability[13,14].

The acidity of S1, S2 and S3 were analyzed with NH_3-TPD and the results are shown in Fig. 3. As shown in Fig. 3, the NH_3-TPD and pyridine-TPD acidity of support S2, which was prepared by adding carbon black and calcinating at high temperature, is lower than that of normal support S1 and drastically lower than S3. The NH_3-TPD acidity and acid distribution of S1 and S3 were approximately the same, but the mild and moderate pyridine-TPD acidity of S3 was higher than S1. Since the molecular diameters of NH_3 and pyridine are 2.6 and 6.5 Å, respectively, the pores size of S2 were larger than S3, but the acidity was lower after calcinating at a higher temperature. The pores of S3 were clearer, which means that the active sites that encourage the adsorption and reaction of large molecular reactants were increased and this is beneficial for removing macromolecular sulfides.

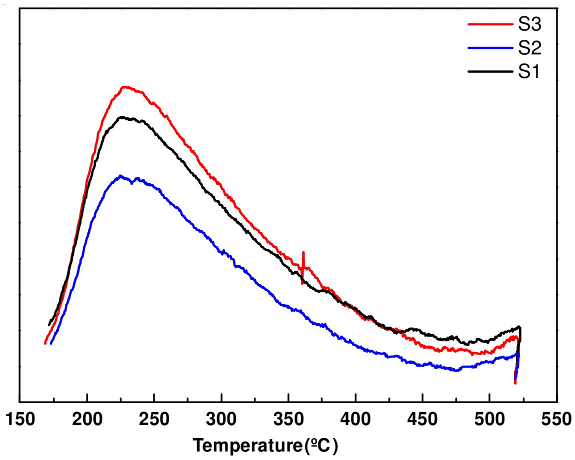

Fig. 3. NH_3-TPD profiles of different supports

Finally the effects on degree of sulfurization of different catalysts are given in Table-4.

TABLE-4
EFFECTS ON DEGREE OF SULFURIZATION
OF DIFFERENT CATALYSTS

Catalysts	C1	C2	C3
Supports	Support S1	Support S2	Support S3
Sulfur (%)	7.80	7.34	9.22
Sulfurization degree (%	73.6	69.2	87.0

Conclusion

- Compared to conventional supports, the new alumina supports have a larger pore volume, higher specific surface area and larger pore diameter. Additionally, the pore is clearer, which is beneficial to the adsorption-desorption of macromolecular sulfides.
- Compared to conventional supports, the acidity analysis results with NH_3 and pyridine, whose molecular sizes are different, show that the new supports prepared through mild and moderate acid have more active sites, are beneficial to adsorption of macromolecular sulfides and even improve intrinsic activity.
- Developing suitable catalysts with pore sizes and stable acidity was beneficial to the sulphurization of active metals and the removal of macromolecular sulfides with strong steric effects, such as 4,6-DMDBT. Furthermore, improving the catalytic activity of HDS and HDN for treating heavy diesel fractions is the key goal in the research of catalysts. When heavy straight-run diesel was treated, the reaction temperatures of the new catalysts were 10 ºC lower than the reference catalysts prepared by conventional supports. These results indicate that catalysts prepared with these new supports are effective in removing macromolecular sulfides impurities.

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