Hydrodesulfurization of DBT on NiMo catalyst supported on γ-Al_2O_3

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Abstract

NiMo/Al_2O_3 catalysts prepared by impregnation and co-precipitation methods have been compared in the influence degree by the operation conditions for the hydrodesulfurization of dibenzothiophene (DBT). The results showed that there are similar change trends with the operation parameters vary, but the operation conditions effect on the precipitation catalyst is smaller than that on the impregnation catalyst. On the same reaction parameters, the activity of precipitation catalyst is superior to the impregnation catalyst.

Keywords

NiMo/ Al_2O_3 catalysts, Impregnation method, Co-precipitation method.

1. Introduction

The maximum amount of sulfur allowed in gasoline and diesel fuel was reduced to 10 ppm in national VI gasoline quality standards. Deep hydrodesulfurization(HDS) technology must be implemented to attain this low level of sulfur[1]. Studies have shown that the use of conventional hydrotreating catalysts for deep desulfurization of diesel in traditional diesel hydrotreaters would require severe operating conditions such as high temperature, low space velocity and high hydrogen partial pressure. Such severe processing conditions generally lead to rapid catalyst deactivation, shorter cycle lengths and reduced throughput and under these working conditions the oil upgrading cost increases considerably[2]. Taking cost requirements into consideration, a reaction temperature below 623 K and a reaction pressure of H_2 below 3.5 MPa would be preferable. So, strict regulation of the sulfur content in fuels is the driving force for further research and development of more active catalysts[3].

In order to achieve more active catalysts many approaches have been followed. The first one is based on the use of some additives in the catalyst formulations. Phosphorus[4], fluorine[5] and boron[6] are the three important additives that have been investigated extensively. The second approach is to use new supports. A large number of new materials with high surface area and other suitable properties have been developed and tested. The third approach concerns the preparation methods. The method of preparation is one of the fundamental factors that plays an important rule in the precursor structure and consequently in the activity of hydro-processing[7].

There are many methods for catalyst preparation, such as impregnation, precipitation, decomposition of metal sulfur compounds, metathesis reaction, and sonochemical preparation[8,9]. As a conventional catalyst preparation method impregnation has been extensively used by commercial catalyst manufacturers. There are two intrinsic disadvantages resulting from the impregnation method: (1) the lack of uniform particle and active species distribution because of forced condensation of metal precursors on the support surface during the drying process and (2) limited activity because of the restrained amount of active metals deposited on support surface. In contrast, another traditional method precipitation has a potential to avoid the drawbacks resulting from impregnation method.

In our previous work[2], the bulk-phase composition, surface area, pore volume, and particle size distribution, surface chemical bonding states and the morphology of the NiMo/γ-Al_2O_3 catalysts which prepared by impregnation and co-precipitation methods were compared on the results of XRD, BET, XPS and SEM. In the present work, we have studied the performance of NiMo catalysts, in which attention was focused on the influence of preparation technique and operation parameters effect on the different catalyst prepared through impregnation and precipitation. Systematic experiments were conducted to investigate the following: (1) the effect of operating conditions on the conversion of DBT; (2) the influence of process conditions on the extent of the production of DBT HDS; (3) determine the kinetics of DBT HDS catalyzed by Ni-Mo/γ-Al_2O_3 using a high pressure flow micro-reactor under deep desulfurization conditions.

2. Experimental

2.1 Reagents

Reagents used in this work included DBT (98%, Sigma-Aldrich), carbon disulfide (98%, Xilong Chemical Factory), decahydronaphthalene (98%, Sinopharm Chemical Reagent Co. Ltd.), cyclohexylbenzene (99.5%, Shengqi Chemical Factory), and biphenyl (99.5%, Jinmaotai Chemical Factory). Catalyst was provided by Luknova Inc, without sulfidation. Catalyst consist of 16.5% Mo and 4.4% Ni in MoO_3-NiO/Al_2O_3. A and B was prepared by impregnation and coprecipitation method respectively.

2.2 Apparatus and procedure

The studies were conducted in a trickled-bed reactor of i.d.10mm stainless steel tube using 1.0wt% dibenzothiophene (DBT) as feed. The reactor was considered in steady-state operation with plug flow of gas and liquid phase. Catalyst samples were crushed and sieved to 40-60 mesh granules, to satisfy the criteria for avoiding mass transfer limitation. 1g catalyst sample was diluted with an equal amount of SiC with the same mesh and then loaded into the reactor. Before introduction of the feed, the catalyst was presulfided with 3wt% carbon disulfide in decahydronaphthalene. When the presulfiding was completed, the gas oil feed was introduced and presulfiding feed was stopped. Before performance test, the activity of all catalysts were stabilized by precoking it for 7h at the temperature, pressure, LHSV and H_2/feed ratio of 300℃, 3.0 MPa, 3.0 h^{-1} and 500 mL/mL, respectively. Initially, the activity of NiMo/γ-Al_2O_3 catalyst is very high and unstable and deactivate quickly because of the deposition of coke on the catalyst surface. So, it is important to stabilize the catalyst prior to actual reaction in order to ensure steady state activity on the catalyst surface. After aging the reactor temperature and other conditions were adjusted to the desired start-of-run conditions. Initial experiments were focused on studying the effect of important process variables on the extent of conversion of the DBT feed. The process parameters studied included reactor temperature, hydrogen partial pressure, liquid hourly space velocity and hydrogen-to-oil ratio. *Table 1* summarizes the process conditions used in the present studies.

The stability of the catalyst activity and selectivity was frequently checked by performing experiments at reference operating conditions. Catalyst deactivation and hydrocracking of the solvent decahydronaphthalene did not occur under the conditions mentioned above.

Table 1: Process condition\

Process operation	Temperature	LHSV	H2/oil	Pressure
Temperature(℃)	260~320	280	280	280
Pressure(MPa)	3	3	3	1~4
H2/oil(mL/mL)	500	500	100~500	500
LHSV(h-1)	3.0	3.0~6.0	3.0	3.0

2.3 Analysis

The liquid product collected from a gas-liquid separator were analyzed by off-line gas chromatograph with a flame Ionization detector and an OV-1701(50m × 0.25mm × 0.5µm) capillary column at the column temperature of 250℃, the injection temperature of 280℃ and the detector temperature of 280℃. Each component in liquid products was identified by its retention time compared to those of relevant pore compounds. The catalytic activity was investigated in terms of total conversion and the product selectivity last out 4 h on stream when the conversion reached a steady state. The reproducibility of the catalytic tests was better than 5%. Typically, 7h is allowed at each reaction condition for the catalyst to stabilize.

3. Results and discussion

3.1 Influence of process conditions

According to Arrhenius equation, increasing the operating temperature will favor to improving the speed of reaction. The data presented in Figure 1 show that the overall HDS activity smartly increases with increasing operating temperature in the range 260~300°C on both the catalysts. Accord to the catalyst B, when the temperature changed from 260°C to 270°C, the conversion rapidly increased to 99.63% from 69.23%. Then the temperature increasing has less influence in enhancing the DBT conversion. But in the same conditions, when the temperature increase from 260℃ to 270℃, the DBT conversion only reach to78.29% with the catalyst A. Desired to get the deep desulfurization result that the DBT conversion >95%, the temperature should be increased to 270℃ with the catalyst B but 280℃ on the catalyst A. It is seen that the conversion of DBT reached approximate 100% at 300°C under the set of reaction conditions: LHSV = 3.0h $^{-1}$, H_2/oil ratio =500, P =3MPa over the both catalyst used in the present work.

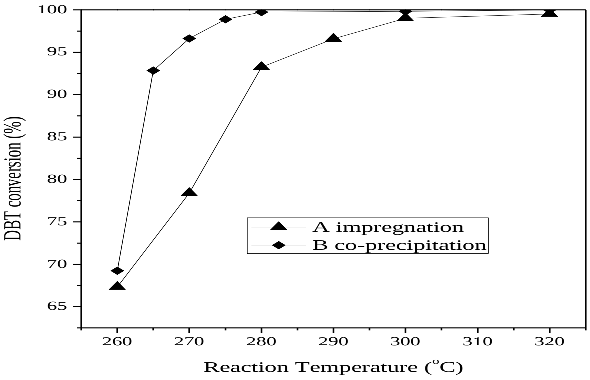


Fig.1 Effect of reaction temperature on the conversion of DBT

Figure 2 indicate that an increase in total pressure leads to a marginal improvement in sulfur removal. The increase of the DBT conversion with reaction pressure, but the change is insignificant due to the achievement of almost complete DBT conversion over catalysts. For example, there is high conversion of DBT (99.45%) when total pressure is 1MPa, so the activity of the theNiO-MoO_3/γ-Al_2O_3 catalyst used in the present work is very splendid. At the same pressure, catalyst A activity is lower than catalyst B. The DBT conversion is just 91.62% with catalyst A and 99.45% over catalyst B at 1.0MPa.

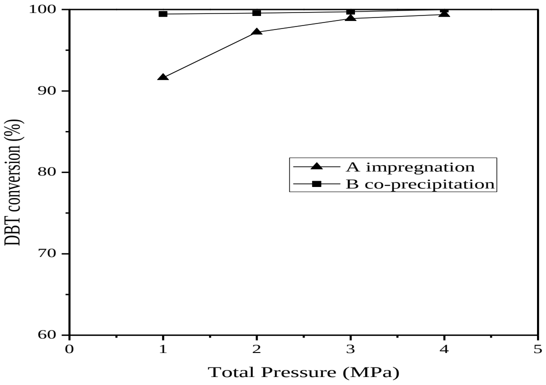


Fig. 2 Effect of total pressure on the conversion of DBT

The H_2/oil ratio has a marked influence on DBT desulphurization (Figure 3). DBT conversion increased with the H_2/oil ratio because, thermodynamically, the presence of high H_2 partial pressure could shift the reaction equilibrium toward the HDS-favored side. We can see from the figure, the effect is more pronounced up to an H_2/oil ratio of 400. At low severity (T=300°C; P =3 MPa;

LHSV=2.76h^{-1}), increasing the H_2/oil ratio from 100 to 400 reduces the sulfur content from 9.87 to 0.28 wt% over catalyst B. So increasing the H_2/oil ratio is available to reduce the sulfur content. But continue increasing the H_2/oil ratio to 500, there is no effect on the conversion of DBT. So the ratio of H_2/oil must be maintained above 300 in order to obtain the best DBT conversion.

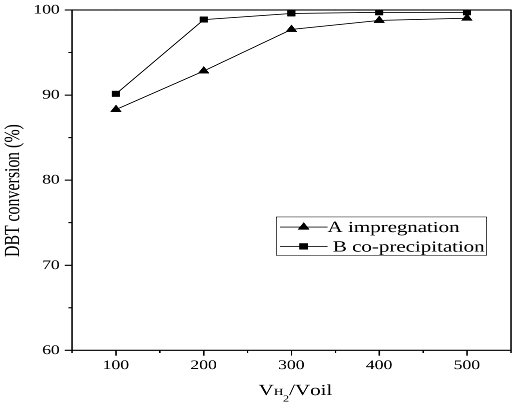


Fig. 3 Effect of H2/oil ratio on the conversion of DBT

Figure 4 illustrates the influence of feed space velocity (LHSV) on the degree of desulfurization. The DBT conversion significantly decreased with LHSV since increasing LHSV reduces the residence time and thus results in the decrease of reactant conversion. At moderate temperature (300°C) and pressure (3MPa) and at an H_2/oil ratio of 500, the LHSV has to be reduced to < 4 h^{-1} to achieve the desired sulfur in the product.

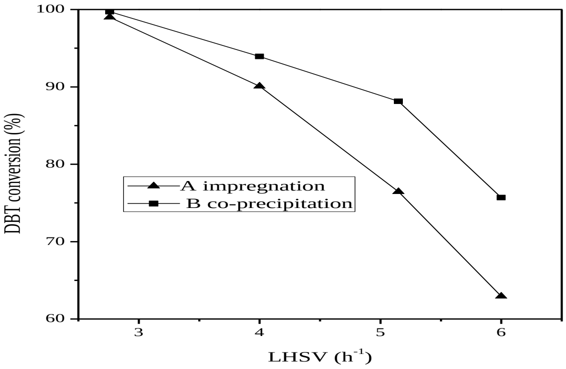
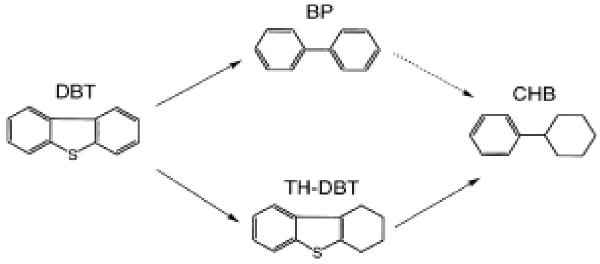


Fig. 4 Effect of LHSV on the conversion of DBT

The results of the present studies reveal that the deep hydrodesulfurization is considerably influenced by operation temperature, space velocity and H_2/oil ratio. Deep desulfurization of gas oil to low-sulfur (10 ppm max) diesel fuel can be achieved by varying any one of these process parameters. However, it should be noted that at relatively high space velocities (e.g. 4 h^{-1}) and low H_2/oil ratios (e.g. < 200), higher operating temperatures (e.g. > 320°C) are necessary to effect deep desulfurization to acceptable sulfur levels (10ppmw max.) in the product. This will reduce the cycle length. The LHSV could be slightly lowered to keep the start-of-run temperature at a moderate level (e.g. 280°C), but this would reduce the throughput. An increase in H_2/oil ratio to ~300 would be necessary to achieve the desired low sulfur levels without sacrificing the cycle length and throughput, and the optimum process conditions appear to be T=300°C; P=3.0MPa; LHSV=2.76h^{-1}, H_2/oil = 400.

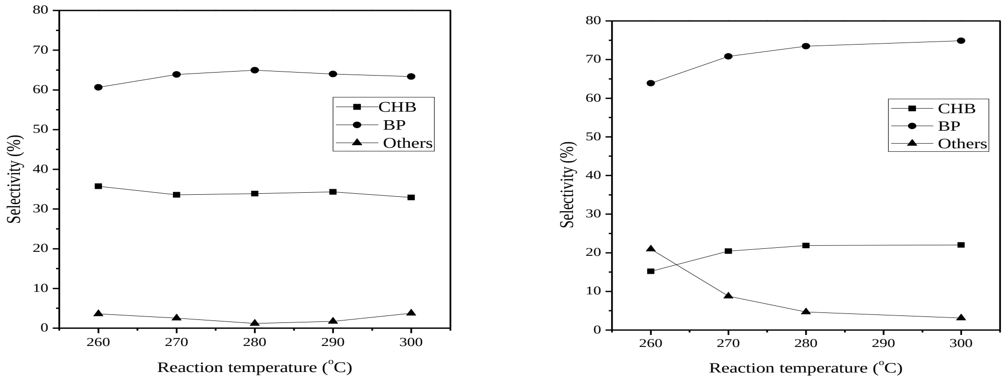
3.2 Selectivity

According to the literature reports[4,10], that cyclic sulfur compounds react through two pathways, viz., the so-called direct desulfurization (DDS) and the hydrogenation (HYD), and that the ratio of DDS to HYD depends on the reactant molecules, the catalysts properties and the reaction conditions. The reaction pathways of DBT are shown in Scheme 1. It is possible to discriminate from the product distribution between DDS and HYD in DBT. As shown in Scheme 1, The hydrogenation route goes to cyclohexylbenzene (CHB) through tetrahydrodibenzothiophene (THDBT), and the direct desulfurization route leads to biphenyl (BP). Moreover, tetrahydro-DBT was observed, supporting the reaction scheme.



Scheme1. Reaction pathways of HDS of DBT

Figure 5 gives the selectivity to cyclohexylbenzene and biphenyl over the catalyst A and B in experiment as a function of reaction temperatures. The results indicate that both the DDS and the HYD pathways are significant for the catalysts our studies, while DDS is slightly more important than HYD under our experimental conditions. The selectivity to biphenyl was approximately 3 times higher than that to cyclohexylbenzene. The selectivity to cyclohexylbenzene and biphenyl were influenced slightly by the temperature in the range from 533 to 573 K.



(a) (b)

Fig.5 Steady-state selectivity of products as a function of reaction temperature with catalyst A (a) and B(b)

The mechanism for the conversion of DBT over various catalysts was the same. Biphenyl was the major HDS product of DBT but a signigicant amount of phenylcyclohexane was also observed to form in a parallel fashion. Indepenent studies showed that the hydrogenation of biphenyl was very slow for these catalysts. This indicates that both direct desulfurization and hydrogenative desulfurization occured. The predominance of hydrogenolysis over hydrogenation is still apparent even at low temperature.

3.3 HDS kinetics

The kinetics of hydrodesulfurization of diesel feedstocks is complex, due to the presence of many kinds of sulfur compounds requiring different rate and reactivity for each reaction. In practice, all desulfurization reactions are usually lumped into a single reaction of sulfur with hydrogen giving hydrogen sulfide as the end product. The pseudo-first-order kinetic model was frequently used to correlate data in HDS of DBT and its derivatives. For individual sulfur compounds such as thiophene, benzothiophene and dibenzoth -iophene, the reaction has been found to be first-order with respect to the sulfur compounds[10]. The integrated rate equation of the pseudo-first-order model for a plug-flow reactor is as follows:

$$-\ln(1-x) = k_{HDS}/LHSV$$

Where x presents the DBT conversion, and k'_{HDS} is the global rate constant (mmol/(L·h).

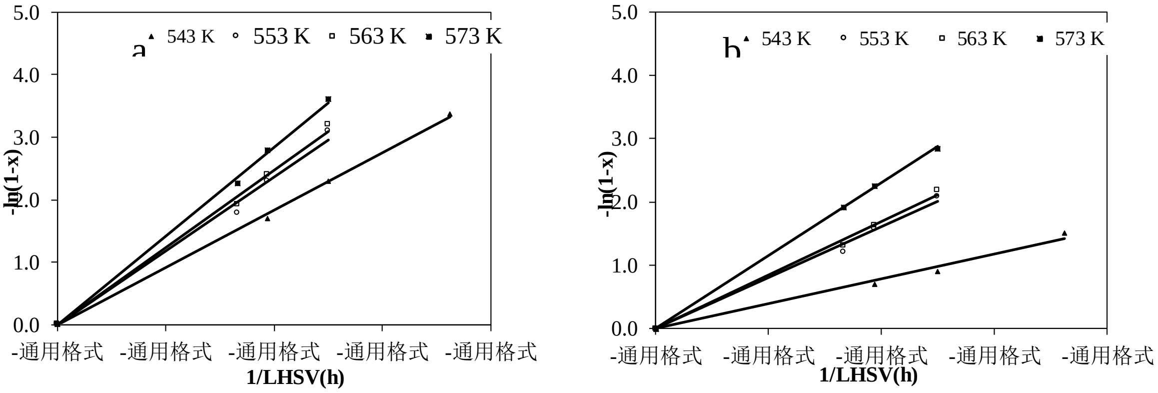


Fig. 6 The $-\ln(1-x)$ plots against 1/LHSV at various temperatures over NiMo/Al2O3 catalysts prepared by co-precipitation (a) and impregnation (b).

According to pseudo-first-order kinetic model, the -[ln(1 - x)] is plotted against 1/LHSV will form a linear which through plot (0,0). -[ln(1 - x)] is plotted against 1/LHSV for HDS reaction catalyzed by Ni-Mo catalyst at different temperatures, as shown in Figure 6.The result showed that the pseudo-first-order model is well fitted to the experimental data at the various temperature.

The kinetic constants of the model are calcuclated according the equation showed in Figure 6. The calculated activation energies for DBT HDS over catalysts prepared by impregnation and coprecipitation are 83 kJ/mol·K and 34 kJ/mol·K, respectively. The activation energy for DBT HDS over coprecipitation catalyst is significantly lower than that over impregnation catalyst, which explains well why the coprecipitation catalyst exhibited higher activity than impregnation catalyst.

4. Conclusion

The experiments revealed that increase of temperature, pressure and H_2/CH ratio as well as decrease of LHSV had positive effect on the HDS of DBT while other process parameters were kept constant.

The kinetic parameters were estimated on the basis of experimental results of sulfur content in the exit reaction mixture. The agreement between the experimental and theoretical values was satisfactory.

Acknowledgements

Boshi Qidong Foundation zksybscx201107.

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