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Catalyst design and development for upgrading hydrocarbon fuels

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Abstract

Hydrogenation and hydrocracking catalysts were designed and synthesized based on findings from catalyst characterization and model reactions. Two types of the synthesized catalysts were then tested using two stage upgrading of unconventional feedstocks. The causes of catalyst deactivation were studied in order to prepare a practical catalyst with a long life.

1. Introduction

Consumption of transportation fuels is increasing continuously, while heavy oil consumption is decreasing gradually. Since the reserves of conventional crudes are declining, there is a strong need to convert hydrocarbon feedstocks into lower boiling point products in greater yields and with more selectivity. Unconventional feedstocks, which typically contain aromatics and high concentrations of organic nitrogen and sulfur compounds, have to be hydrocracked into lighter fractions. Although hydrocracking processes and catalyst technologies are improving [1], the regulations governing hetero-atoms and aromatic content in fuels are becoming increasingly severe to minimize air pollution. Until recently most regulations on diesel fuel were only concerned with sulfur content. Now, reduction of aromatic content is also required since aromatics contribute significantly to the formation of particulate emissions in exhaust gases. As a result of the tightening of the regulations, there is now great interest in the research and development of processes and suitable catalysts for hetero-atoms removal and aromatics reduction in middle distillates [2].

2. Strategy of catalyst development

Since unconventional feedstocks contain large amounts of aromatics and hetero-atoms, insufficient hydrocracking of aromatics occurs in a one-stage process. A two step hydrocracking process provides more efficient conversion of polyaromatic hydrocarbons in middle and heavy distillates to lighter fractions. In the first step the polyaromatics are hydrogenated and in the second step these reduced aromatics are hydrocracked. Fundamental catalytic functions of hydrotreating catalysts are hydrogenation (HY) and

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hydrocracking (HC). Thus, two kinds of catalysts, each possessing higher hydrogenation or hydrocracking activity, are required for producing clean fuels from heavy hydrocarbons [3,4].

The objective of this article is to introduce the design of hydrotreating catalysts based on an understanding, derived from fundamental research, of the physical properties such as the support effect, nature of active sites and changes in local structures of active metal during reaction.

3. Hydrogenation and hydrocracking catalysts

In this work various kinds of hydrogenation and hydrocracking catalysts were prepared using an impregnation method. Alumina, titania, silica, zirconia and double oxides such as SiO_2–Al_2O_3, TiO_2–Al_2O_3 and ZrO_2–Al_2O_3 were used as supports of the hydrogenation catalysts, while some kinds of zeolites and double oxides were selected for the preparation of the hydrocracking catalysts. Mesoporous carbon was not applied to the support due to lower surface area and poor crushing strength. The active metal combinations selected were Ni–Mo, Co–Mo and Ni–W. The total active metal loadings on the catalysts were varied from 2 wt.-% to 30 wt.-% as MoO_3. After impregnating supports with aqueous solutions of active metals, the catalysts were subsequently dried at 110°C for 10 h and calcined at 500°C for 3 h. Although carbide and nitride catalysts have been reported to have superior activities [5], we used sulfide catalysts since they could be more easily prepared with a large surface area.

After presulfiding the catalysts in a stream of 5 vol.-% H_2S (H_2 balance) at 200–500°C, model reactions using 1-methylnaphthalene and diphenylmethane were carried out to evaluate, respectively, HY activity of aromatic rings and HC activity of C–C bond. Each catalyst was characterized using TEM, XAFS, XPS, Raman spectroscopy and thermal analyses in order to understand the relationship between the catalyst functions and their properties. From these results two types of catalysts were designed and prepared. The two new kinds of catalyst were then used to catalyze two-stage upgradings of unconventional feedstocks. The factors resulting in catalyst deactivation were examined in order to prepare a practical catalyst with a long life.

3.1. Support effect

It is known that the interaction between support and active metal is support dependent. XAFS, XPS and Raman spectroscopy revealed

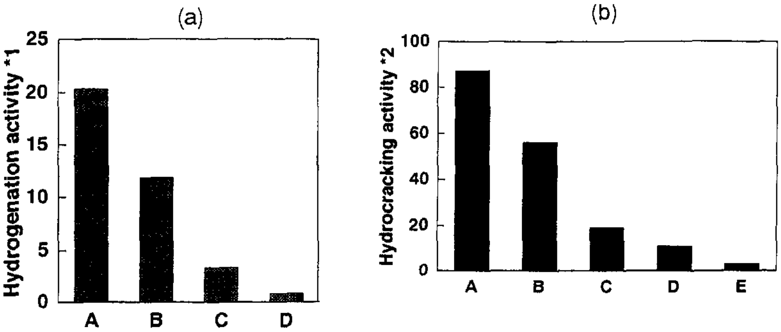

Fig. 1. Hydrogenation and hydrocracking activities of molybdenum sulfide catalysts over various supports. (a) Hydrogenation; A, Al_2O_3; B, TiO_2; C, ZrO_2; D, SiO_2. (b) Hydrocracking; A, Y-zeolite; B, Mordenite; C, ZSM-5; D, SiO_2–Al_2O_3; E, Al_2O_3. * 1 Total yield of 1- and 5-methyltetralin. * 2 Total yield of benzene and toluene. 1-methylnaphthalene and diphenylmethane were used as model compounds for evaluating hydrogenation and hydrocracking activities, respectively. 10 wt.-% of MoO_3 was supported on each support. Reaction conditions of batch reactors are as follows; H_2 initial pressure, 6.9 Mpa; Reaction temperature, Hydrogenation 350°C, Hydrocracking 400°C; Catalyst, 0.3 g; Reaction time, 1 h.

that each support gave different dispersion and local structure to the active metal [6]. As expected, catalyst functions were influenced by the support [7]. Al_2O_3 support gave the highest HY activity among various single oxide supports (Fig. 1a). This is mainly due to the large surface area and pore volume of the Al_2O_3 support compared to the other supports. Although the SiO_2 support possesses a larger surface area than the Al_2O_3 support, less interaction between the support and active metal leads to more sintering of the active metal on the catalyst, resulting in lower HY activity. In the case of TiO_2, ZrO_2 and double oxides supports, precise control of the physical properties such as pore volume or surface area to meet the necessary requirements was difficult. It is likely, however, that the physical properties of these single or double oxides supports can be improved in the future [6]. The support component of hydrocracking catalysts can be of two major types: (1) an amorphous double oxide support such as silica–alumina and (2) a mixture of a crystalline zeolite and amorphous oxide support. Research using model reactions has indicated that catalysts based on Y-type zeolite are suitable for cleavage of hydrogenated aromatic rings (Fig. 1b). Because catalysts based on Y-type zeolite have been found to be much more active than catalysts based on double oxides or other zeolites such as mordenite or ZSM-5, we decided to use Y-type zeolite for the hydrocracking catalysts. Further, since the Y-type zeolite must be thermally stable and nitrogen-tolerant, the basic synthesized zeolites (silica/alumina ratio = 5) were highly modified. Dealuminated USY-type zeolite was applied to prepare a support of hydrocracking catalysts. A mixture of USY (30–60 wt.-%) and Al_2O_3 (70–40 wt.-%) was selected because of its superior HC activity.

3.2. Active metals and active sites

An increase in catalytic activity was generally observed when the active metal loading was increased. The HY activity of the catalyst increased until a monolayer of metal sulfide was formed on the catalyst surface and then began to decrease gradually (Fig. 2a) [8]. Remarkable increases in HC activities of the catalysts were obtained when higher amounts of active metals were loaded (Fig. 2b), suggesting that the ratio of HY to HC active sites was changed when the active metal loading was varied. The average lateral size of the MoS_2 slabs on the catalysts increased with Mo loading. At high metal loadings, multiplication of MoS_2 slabs was observed on the catalysts. Co was effective for the multiplication of MoS_2 slabs. The lateral size of the MoS_2 slabs increased in the order Co–Mo < Mo < Ni–Mo at the same total metal loading. In order to understand the correlation between catalytic structure and function, the nature of HY and HC active sites were investigated [9]. It was found that edge sites around the bottom MoS_2 slabs directly bonded with Al_2O_3 support were effective as HY active sites, while edge sites of other MoS_2 slabs, which do not have direct interaction with the support function, were effective as HC active sites.

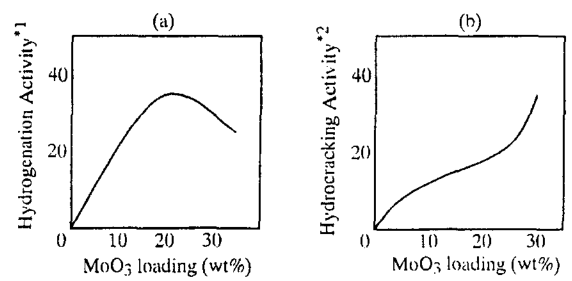

Fig. 2. Hydrogenation and hydrocracking activities of molybdenum sulfide catalysts as a function of Mo loading. (a) Hydrogenation, (b) Hydrocracking. * 1 Total yield of 1- and 5-methyltetralin. * 2 Total yield of benzene and toluene. Reaction conditions are the same as described in Fig. 1. Molybdenum loading was varied from 2.5 to 30 wt.-% as MoO_3, while Al_2O_3 was used as the support of molybdenum sulfide catalysts.

Traditionally, the active species of hydrogenation catalysts have been selected from transition (Co–Mo, Ni–Mo, Ni–W) and noble metals (Pd, Pt, Ru). Since noble metal catalysts are easily deactivated by organo–sulfur components and hydrogen sulfide, these catalysts can only be used with sulfur-free feeds. The order of HY activities of sulfide catalysts was Ni–W > Ni–Mo ≫ Co–Mo. However, the HY activity of the Ni–W catalyst was greatly decreased when sulfur was present in the feeds. The HY activity of the Ni–Mo catalyst was less sensitive to sulfur-deactivation. Thus, the choice of hydrogenation catalyst depends on the concentration of sulfur in the feed [10]. For the first-stage upgrading, catalysts with higher HDN and HY activities are required, since organo–nitrogen compounds have adverse effects on the zeolite catalysts used in the second-stage reaction.

For hydrocracking catalysts, proper active metal loading is necessary for improving HC activity and for reducing carbonaceous deposits on the catalyst. For the catalyst used in the second-stage upgrading Ni and W were selected as active metals, because most of the sulfur in the feed was removed in the first-stage upgrading.

3.3. Sulfiding

The HY activities of molybdenum sulfide catalysts were proportional to the degree of active metal sulfiding (Fig. 3a). The sulfide form of Mo was almost as efficient as the various Co–Mo and Ni–Mo catalysts prepared, when the same active metal loading and presulfiding condition were used. While the sulfiding behavior of W on tungsten sulfide catalysts was quite different from that of Mo on the molybdenum sulfide catalysts, W was less sulfided than Mo at lower sulfiding temperatures. The crystal growth of WS_2 like structures occurred more easily than that of MoS_2 like structures at higher sulfiding temperature, resulting in a considerable decrease in the number of HY active sites. This is probably due to the smaller interaction between W and Al_2O_3 as compared to that between Mo and Al_2O_3. Similarly, the sulfided states of W and Mo, which had the highest HY activities of Ni–W or Ni–Mo catalyst, was different from each other (Fig. 3b). These results clearly show that the HY activity of the Ni–W catalyst greatly increase if the sulfiding of W is controlled in order to minimize the growth of WS_2 crystals.

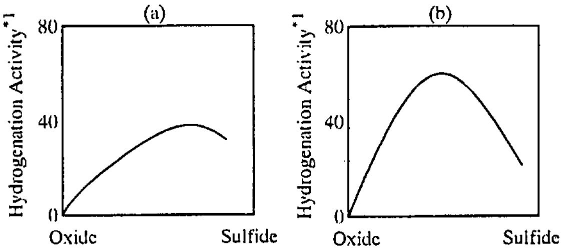

Fig. 3. Hydrogenation activities of Ni–Mo and Ni–W catalysts as a function of active metal sulfiding. (a) 3 wt.-% NiO–15 wt.-% MoO_3/Al_2O_3, (b) 3 wt.-% NiO–24 wt.-% WO_3/Al_2O_3. *1 Total yield of 1- and 5-methyltetralin. Before reactions XPS was used for evaluating the degree of active metal sulfiding. Reaction conditions except reaction temperature are the same as described in Fig. 1. Reaction temperature used is 310°C.

4. Catalyst preparation

Ni–Mo and Ni–W/Al_2O_3 catalysts were designed and prepared for the hydrogenation catalyst. The physical and chemical properties of the Al_2O_3 support such as pore structure and acidity were controlled to enhance the acidity of the active metals on the surface by changing preparation conditions. Then each metal loading and presulfiding of Ni–Mo and Ni–W catalysts was optimized to give the highest HY activity.

During the preparation of the hydrocracking catalyst, we experimented with various active metals and found that the Ni–W/zeolite (60 wt.-% USY and 40 wt.-% Al_2O_3) was the most active among the Ni–W, Ni–Mo and Co–Mo/zeolite catalysts. Hence, Ni–W/USY-zeolite–Al_2O_3 was selected for the hydrocracking catalyst. The physical and chemical properties of USY-zeolite such as SiO_2/Al_2O_3 ratio, pore size distribution and acidity were modified to enhance the HC activity. Then each metal loading and sulfiding of the Ni–W/Y-zeolite catalyst was optimized to give the highest HC activity.

The synthesized hydrogenation and hydrocracking catalysts were evaluated using model reactions. Superior catalytic functions were obtained for both catalysts compared to commercially available catalysts.

5. Two stage upgrading

Two kinds of catalysts, each possessing one of two types of catalytic functions defined above, were used for a two-stage upgrading of coprocessing oil, coal-derived liquids and light cycle oil. Catalysts that had shown the highest catalytic performance for hydrogenation and hydrocracking were selected from commercially available catalysts as reference catalysts. The hydrogenation and hydrocracking catalysts designed and prepared in this work gave higher HY and HC activities for upgrading unconventional feedstocks as compared to the reference catalysts. The Ni–Mo/Al_2O_3 catalyst showed higher HY and HDN activities than the Ni–W/Al_2O_3 catalyst for the first-stage upgrading of the coprocessing oil and the light cycle oil. However, higher HY and HDN activities were observed over the Ni–W catalyst as compared to the Ni–Mo catalyst for the first-stage upgrading of coal-derived liquids. The difference is due to the sulfur concentration in the feed. Very low nitrogen content in the feed was essential for the second-stage upgrading over the zeolite catalyst. Low sulfur content was also required for stable catalyst performance of the Ni–W/zeolite catalyst. This two-stage process and the application of the newly developed catalysts showed considerable improvements in overall activity and initial deactivation, compared to conventional one stage process and the application of commercial catalysts. When optimized catalysts were used in the first-stage and second-stage upgrading, lighter fractions with less amounts of hetero-atoms and aromatics, were efficiently produced from unconventional feeds.

6. Catalyst deactivation and new catalyst design

Based on a better understanding of deactivation phenomena, a new type of catalyst with a longer life can be designed for practical usage in hydrotreating petroleum and synthetic heavy oils [11]. Deactivation of the Ni–W/Al_2O_3 catalyst used for the first-stage upgrading was not observed during the 1000 h upgrading reaction (Fig. 4a). However, precise characterization of the Ni–W catalyst revealed that crystal growth of WS_2-like structures, changes in the sulfide states and local structures of W, and release of Ni from edges of WS_2 had occurred during the reaction. The model reactions confirmed these changes by showing that the HY and HC activities of the catalysts had decreased after 1000 h of reaction. These findings gave new insight into how to improve the catalytic activity and life of the catalyst. This lead to the following concepts in catalyst design: (1) proper interaction between metal and support for reducing the crystal growth, and (2) stabilization of the Ni–W catalyst surface for reducing of Ni release. The results of the accelerated aging test of catalysts designed on these concepts showed considerable improvement in catalyst life (Fig. 4b).

The HC activities of the Y-zeolite catalysts decreased gradually during the second-stage up-

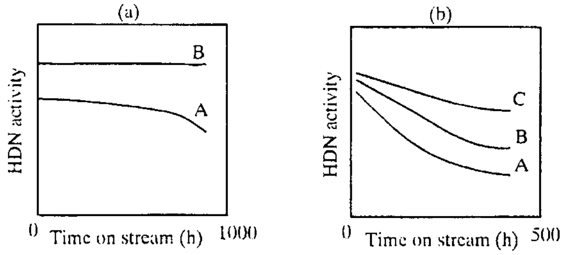

Fig. 4. HDN activities of Ni–W catalysts during a short term life test and an accelerated aging test. (a) A short time life test: A, Reference catalyst; B, Ni–W catalyst prepared. (b) An accelerated aging test: A, Reference catalyst; B, Ni–W catalyst prepared; C, Improved Ni–W catalyst. Reaction conditions are as follows; H_2 pressure, 6.9 Mpa; Reaction temperature, 370°C; LHSV, 2 h^{-1}; H_2/oil, 1000 Nm^3/l; Feed, coal-derived gas oil. Quinoline was added into feed for the accelerated aging test.

grading. Fundamental research on the preparation of well crystallized Y-type zeolite with a high framework Si/Al ratio has to be done for developing a highly active hydrocracking catalyst with a long life. Proper control of the exterior surface and crystal size of the Y-zeolite is very important in hydrocracking.

High silica NaY-type zeolites (silica/alumina ratio = 7) were synthesized using crown-ethers as templates. Then, H-form of the zeolites was prepared by NH_4^+ ion exchange. The protonated form was obtained after calcination of the NH_4-form at 550°C. The high silica Y-zeolites were much more stable during the ion exchanges. Na was more easily removed from the high silica NaY zeolites without loss of crystalline structure compared to commercially available Y-zeolites (silica/ alumina ratio = 5). The high silica HY zeolites showed higher HC activities in the model reactions at lower temperature than the commercially available HY zeolites, indicating that new hydrocracking catalysts prepared using the high silica HY zeolite posses superior HC activity as well as longer life.

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