Catalysis Today 164 (2011) 204–208

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Development of zeolite hydrocracking catalyst and system for resid hydrodesulfurization unit

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ARTICLE INFO

Article history:
Received 15 June 2010
Received in revised form 25 October 2010
Accepted 26 October 2010
Available online 30 November 2010

Keywords:
Resid hydrocracking
HDS
Fixed bed
Zeolite
Catalyst

ABSTRACT

Idemitsu Kosan Co., Ltd. had developed the iron (Fe) containing zeolite catalysts for the fixed bed residual oil (resid) hydrodesulfurization (HDS) unit. The catalysts, named R-HYC, showed high resid hydrocracking (HYC) activity by increasing the middle distillates and concurrently decreasing the bottom fuel oil. Commercial application with resid HDS units had been realized in 1980s–1990s. Because of relatively less HDS activity of R-HYC, the catalyst has been replaced with commercial HDS catalysts to correspond the lowering sulphur regulation in recent years. In order to meet the present demands on refineries, such as coping with the soaring oil price and shrinking market for fuel oil as the primary energy sources, we resumed developing new R-HYC catalysts, which should have good abilities in both HYC and HDS. For more practical purpose to be applicable to the existing atmospheric residue desulfurization (ARDS) unit, a suitable combination for the R-HYC catalyst with the conventional hydrotreating catalysts, such as hydrodemetallization (HDM) and HDS, has been under investigation.

1. Introduction

The catalytic hydrotreating process refers to the upgrading of oil products by means of a treatment with high pressure H_2 at temperature around 400 °C (673 K) in the presence of catalysts. With regard to the objectives the hydrotreating processes can be classified into two categories. One is the treatment that removes carbon-bonded impurities, such as sulphur, nitrogen, and metals, via hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodemetallization (HDM), where HDS is the most important for industrial refining processes. The other is the treatment that improves the properties of oil products and thus provides the additional values on the products, which is known as hydrogenation and hydrocracking (HYC). Most of the residual oil (resid) hydrodesulfurization units have been operated so as just for HDS reaction, while the other reactions like hydrocracking are held in concurrence within the resid HDS reactors. In the meantime, Idemitsu Kosan Co., Ltd. had developed the iron (Fe) containing zeolite catalysts, named R-HYC, and applied the developed R-HYC catalysts to the resid HDS units in Idemitsu-Chiba refinery [1] during between 1982 and 1995 and in Valero refinery [2] during between 1989 and 1997 in USA. Typical catalytic activity of the R-HYC compared with the conventional HDS catalyst is shown in Fig. 1. The R-HYC exhibited higher atmospheric residue (AR) conversion at temperature more than 390 °C. A typical appearance of the resid HDS unit with the R-HYC catalyst in Idemitsu-Chiba refinery is shown in Fig. 2, where the R-HYC was loaded at the upper bed in the last reactor so as to be at higher temperature suitable for the cracking activity.

In recent years, because of relatively less HDS activity of R-HYC, the catalyst has been replaced with commercial HDS catalysts to correspond the lowering sulphur regulation. Nonetheless in order to meet the present demands on refineries, such as coping with the soaring oil price and shrinking market for fuel oil as the primary energy sources, we resumed developing new R-HYC catalysts, which should have good abilities in both HYC and HDS activities and can be applicable to the existing atmospheric residue desulfurization (ARDS) unit. The other prerequisites for the ARDS are hydrodeasphalting (HDAs), hydrodemetallization, and hydrodearomatization (HDAr) or HDCCR, activity to decrease the content of the Conradson carbon residue (CCR), because ARDS units have been employed as pre-treatment for the fluid catalytic cracking (FCC) and residue FCC (RFCC) processes. For this purpose, a suitable combination for the R-HYC catalyst with the conventional hydrotreating catalysts, such as HDM and HDS, has been under investigation.

2. Experimental

2.1. Catalyst preparations

The resid hydrocracking (R-HYC) catalysts used in this study were prepared by impregnating nickel (Ni) or cobalt (Co) and

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doi:10.1016/j.cattod.2010.10.082

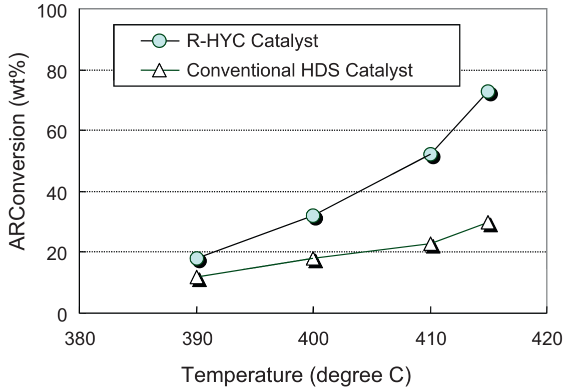

Fig. 1. Atmospheric residue (AR) conversions of the R-HYC and the conventional HDS catalysts. Feedstock: AR-KW, condition: LHSV = 0.3 h^{-1}, pressure (H_2) = 13 MPa.

molybdenum (Mo) on carriers consisting of Fe-supported steaming Y-zeolite (Fe-SHY) [3,4] and alumina. For conventional HDM and HDS catalysts, commercially available catalysts from JGC Catalysts and Chemicals Ltd. (JGC C&C) were used as references, and some of these HDM and HDS catalysts were utilized as pre- and post-treating catalysts in combination with the R-HYC catalyst.

2.2. *Activity evaluations*

The resid hydrocracking experiments were carried out using bench scale fixed bed reactors, where a single type of HDS or R-HYC catalyst was loaded at volume of 100 ml. Each experiment was performed at a hydrogen pressure of 13 MPa, a liquid hourly space velocity (LHSV) of 0.3 h^{-1}. In the case of sequential combinations of the HDM, HDS and R-HYC catalysts at total volume of 250 ml, semi resid HDS unit activity tests were executed using a bench scale fixed bed reactors, at a hydrogen pressure of 13 MPa, LHSV of 0.2 h^{-1}. The properties of the feedstocks, atmospheric residues of Kuwait (AR-KW), Arabian Light (AR-AL) and Arabian Heavy (AR-AH), are listed in Table 1. The produced oil was distilled into LPG, naphtha (pentane to 157 °C), kerosene and gas oil (157–343 °C), AR (over 343 °C), and followed by evaluating the properties of each fraction.

2.3. *Catalyst characterizations*

Pore-size distributions of the supports and the catalysts were measured by Hg intrusion method, and the surface areas and the pore volumes were determined by N_2 adsorption. Degrees of mixing of the zeolite crystallites (Fe-SHY) with alumina carrier were checked with line analyses of both Si, as the main ingredient of Fe-SHY, and Al for cross sections of the catalyst's pellets by electron probe micro analysis (EPMA). Information for the impregnated metals, such as dispersions and the metal–support interactions, were evaluated by temperature-programmed reduction (TPR) [5].

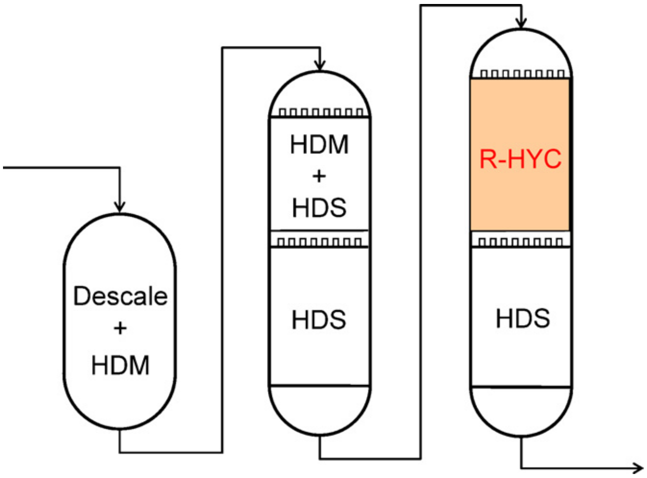

Fig. 2. Appearance of resid HDS unit with the R-HYC catalyst in Idemitsu-Chiba refinery.

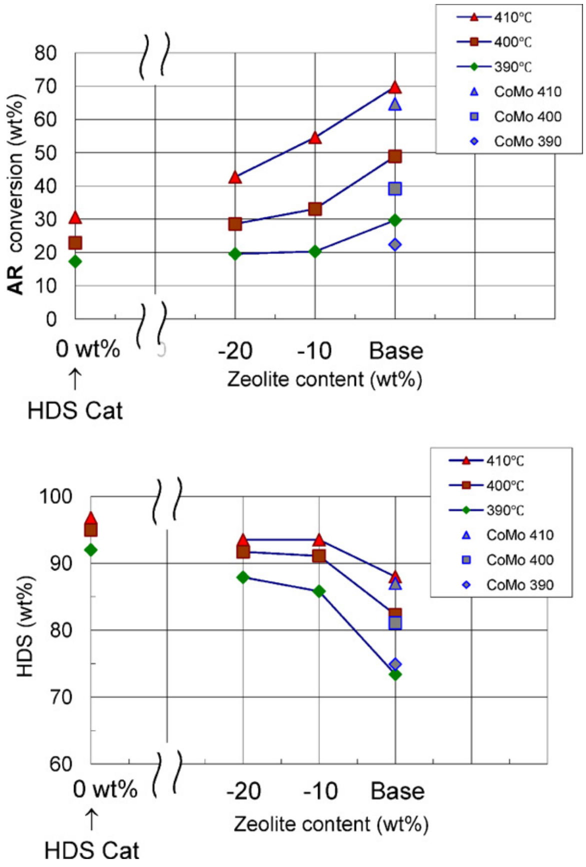

Fig. 3. Effect of zeolite (Fe-SHY) content in NiMo-type R-HYC catalysts on AR conversion and HDS activity, compared with the CoMo-type R-HYC catalyst (existing R-HYC catalyst, whose zeolite content is defined as "base"). Feedstock: AR-AH, condition: LHSV = 0.3 h^{-1}, pressure (H_2) = 13 MPa, H_2/oil = 1,000 N m^3/kL.

3. Results and discussion

3.1. *Search for the improved R-HYC catalyst*

In the same way as so called bifunctional hydrocracking catalysts [6], the existing R-HYC catalyst had been composed of both a carrier consisting of a certain amount of the zeolite (Fe-SHY) mixed with alumina and impregnated CoMo as metal sites. Because of superior activities, especially for AR conversion, as shown in Fig. 3,

Table 1
Properties of atmospheric residues (ARs) used in this study.

Property	Unit	AR-KW	AR-AL	AR-AH
Specific gravity	g/ml	0.975	0.977	0.994
Sulphur	wt.%	4.2	3.4	4.4
Nitrogen	wt.ppm	2100	2000	2720
CCR[a]	wt.%	12.4	10.7	14.1
V	wt.ppm	57	39	86
Ni	wt.ppm	17	10	27
Asphaltens[b]	wt.%	3.9	2.9	7.9

[a] Conradson carbon residue (ASTM D-189).
[b] Heptane (C7) insolubles.

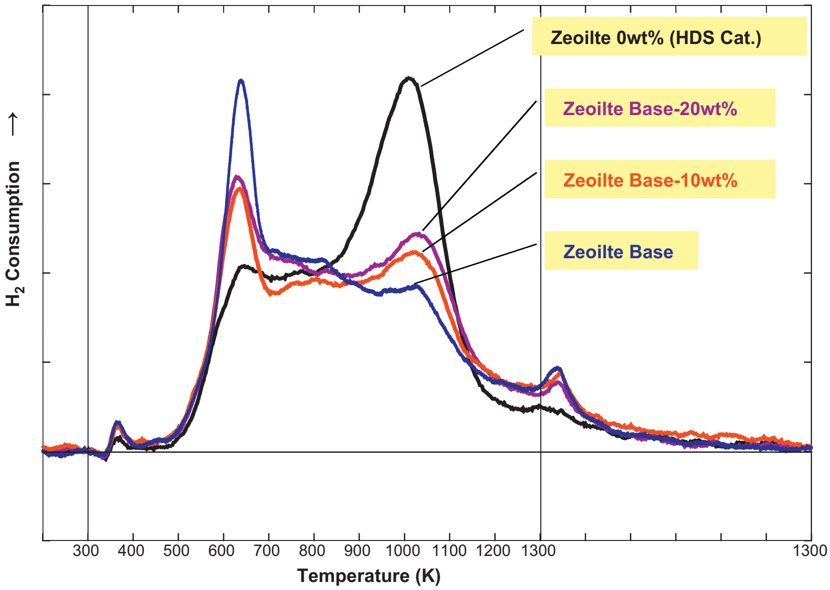

Fig. 4. Temperature-programmed reduction (TPR) patterns for the NiMo-type R-HYC catalysts with different zeolite contents of the supports.

NiMo was chosen as an impregnated metal species instead of CoMo in this study.

The zeolite (Fe-SHY) content of the support is undoubtedly a crucial factor to the catalytic activities. A systematic investigation on effect of the Fe-SHY contents to activities of the NiMo type R-HYC catalysts, as shown in Fig. 3, clearly demonstrated that higher Fe-SHY content had a direct effect on higher AR conversion. On the other hand, higher Fe-SHY content was adversely affected on the HDS activity. In order to keep both the AR conversion and the HDS activities at higher levels, we have selected a suitable Fe-SHY content to “base - 10 wt.%” for the improved R-HYC catalyst.

For heavy feeds, the catalytic activity is generally improved by adding mesoporosity due to enhanced accessibility to the catalytic active sites, and thus the pore-size distribution of the support should be designed carefully. And furthermore, a degree of mixing of the zeolite (Fe-SHY) crystallites with alumina carrier should be taken into consideration. Another factor to affect the catalytic activity, especially for HDS, is metal (NiMo) species, whose quality is known to be determined by the metal–support interaction. For this object, the TPR patterns of the NiMo-type R-HYC catalysts (Fig. 4) clearly shows that the reduction peaks at ca. 1000 K (highly dispersed (Ni) Mo species interacting with the alumina surface [5]) were decreased in

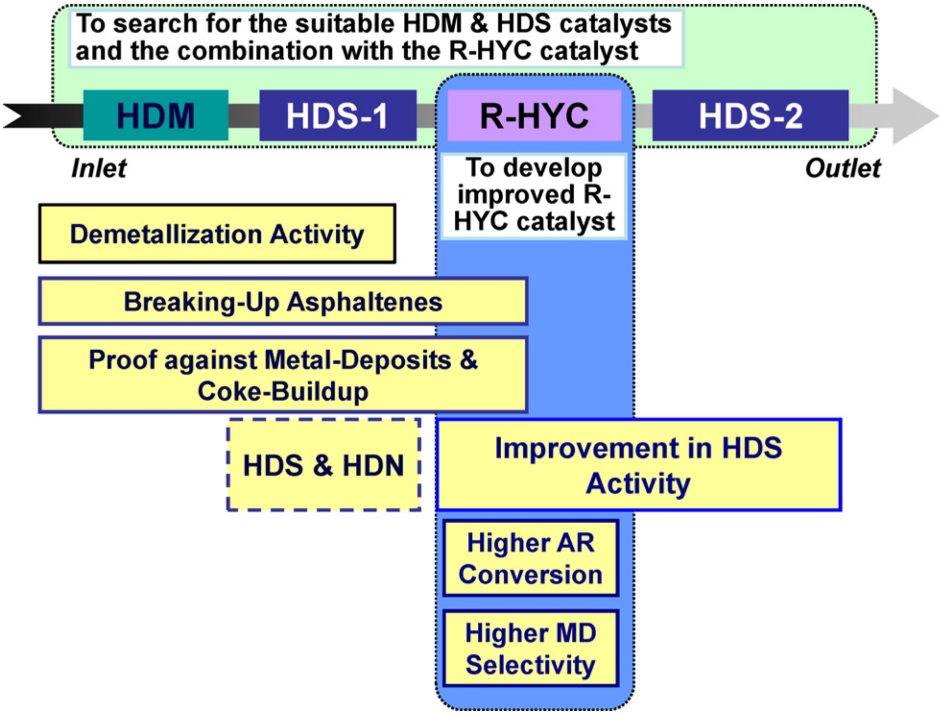

Fig. 5. A typical sequence of the combination of the R-HYC and the other HDM and HDS catalysts applicable to the conventional resid HDS unit, where the role and the point of development for each catalyst is outlined.

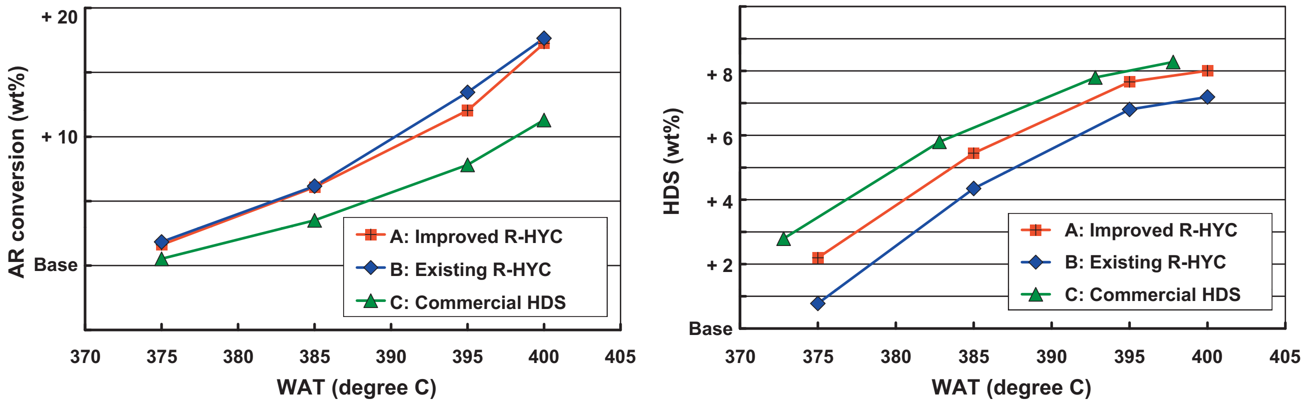

Fig. 6. AR conversions and HDS activities for three different sequences of the catalytic loadings. (A) HDM/HDS-1/improved R-HYC (NiMo/Fe-SHY (base - 10 wt.%))/HDS-2. (B) HDM / HDS-1/existing R-HYC (CoMo/Fe-SHY (base))/HDS-2. (C) HDM/HDS-1/HDS-1/HDS-2. Feedstock: AR-AL, condition: LHSV = 0.2 h^{-1}, pressure (H_2) = 13 MPa, H_2/oil = 900 N m^3/kL.

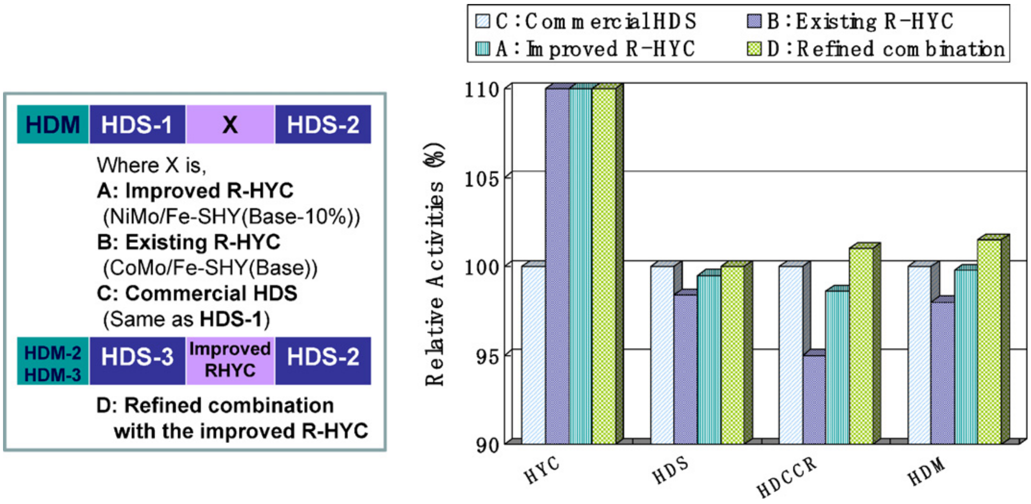

Fig. 7. Relative catalytic activities of four different types of sequential combinations for HYC (AR conversion), HDS, HDCCR, and HDM at a typical condition (395 °C). (A) HDM/HDS-1/improved R-HYC/HDS-2. (B) HDM/HDS-1/existing R-HYC/HDS-2. (C) HDM/HDS-1/HDS-1/HDS-2. (D) HDM-2/HDM-3/HDS-3/improved R-HYC/HDS-2.

intensity with increasing the zeolite contents of the supports as expected.

3.2. *Sequential combinations of the HDM, HDS and R-HYC catalysts*

A typical sequence of the combination of the R-HYC and the other HDM and HDS catalysts applicable to the conventional resid HDS unit, where the role and the point of development for each catalyst is outlined in Fig. 5. In order to compare the improved R-HYC catalyst (NiMo/Fe-SHY (base - 10 wt.%)) with the existing R-HYC (CoMo/Fe-SHY (base)) and the commercial HDS catalysts for their potential usage in the resid HDS unit, three different sequences loading three subjective catalysts with the commercial HDM and HDS catalysts were evaluated. The AR conversions and the HDS activities are shown in Fig. 6. It was clearly demonstrated that the combination-A using the improved R-HYC catalyst exhibited significant increase in the HDS activity compared with the combination-B (using the existing R-HYC catalyst) and getting closer to the combination-C (a commercial HDS combination used in our refinery), while the AR conversion was kept at the same level as the combination-B using the former developed R-HYC catalyst.

For more practical purpose to be applicable to the existing ARDS unit, a suitable combination for the R-HYC catalyst with the conventional hydrotreating catalysts, such as HDM and HDS, has been under investigation. A successful result is shown in Fig. 7, where the combination-D (a refined combination with the improved R-HYC) exhibited the improved activities for HDCCR and HDM compared with the combination-C and can be expected to provide higher quality of DSAR for the existing FCC/RFCC process.

4. Conclusions

Although some experimental results were indicating that improvement of the R-HYC catalyst might be fit for our expectations, the challenge has been launched for developing new hydrocracking catalyst and the system suitable for the existing ARDS unit.

Acknowledgement

This work was supported by the Japan Petroleum Energy Center (JPEC) under a subsidy of the Japanese Ministry of Economy, Trade and Industry (METI).

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