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Hydrocracking of diphenylmethane and tetralin over bifunctional NiW sulfide catalysts supported on three kinds of zeolites

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Abstract

Hydrocracking reactions of diphenylmethane and tetralin were carried out over three kinds of zeolites with or without NiW sulfide to discuss the roles of catalytic bifunctionality in two types of hydrocracking reactions. It was found that strong acid sites were not needed for the hydrocracking of diphenylmethane, while the conversion of tetralin required relatively strong acid sites. Ultra-stable Y zeolite with strong acidity exhibited high hydrocracking activity for both reactions. In contrast, mordenite catalysts did not show high activity for either hydrocracking, though isomerization of tetralin and excess hydrocracking to gaseous products proceeded. The superior performances of ultra-stable Y zeolite in the tetralin hydrocracking were suggested to be related to the hydrogen transfer ability. In most cases, the loading of NiW sulfide enhanced catalytic activity. In the diphenylmethane hydrocracking, the role of NiW sulfide was found to supply active hydrogen to the hydrocracking active sites on zeolite and to prevent polymerization of benzyl cations. In the tetralin hydrocracking, the dehydrogenated products from tetralin were re-hydrogenated over NiW sulfide. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most common heavy oil upgrading process at present is thermal or catalytic cracking, which requires high reaction temperatures over 723 K. This results in further aromatization of feedstocks and deterioration of product quality because of the chemical equilibrium between hydrogenation and dehydrogenation reactions. The other option is catalytic hydrocracking over bifunctional catalysts under 700 K, in which the cracking reactions take place via cation intermediates under high H_2 pressures instead of via radicals. Zeolite catalysts are known to possess high catalytic hydrocracking activity under this temperature range [1].

On the other hand, zeolite catalysts in hydrocracking reactions have serious problems, that is,

1. coke deposition by polymerization of feedstock,
2. active site poisoning by nitrogen-containing compounds or polycyclic aromatic compounds,
3. large production of gases by excess cracking,
4. diffusional limitation of large molecules in micropores of zeolite.

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Our preliminary results indicated that two-stage upgrading might be a solution against these problems [2,3]. In the first stage, the amounts of highly polar matters and condensed polycyclic aromatic compounds are reduced using hydrogenation catalysts, then hydrocracking reactions are carried out in the second stage.

To design a better hydrocracking catalyst for the second stage, it is essential to elucidate the roles of catalyst bifunctionality in the reactions of various kinds of hydrocarbon with different types of C–C bond. From this point of view, we conduct two kinds of model reactions over zeolite based catalysts. Diphenylmethane and tetralin are chosen as model compounds, respectively, for the cleavage of C–C bonds outside aromatic skeletons and for the opening of hydroaromatic rings. As catalysts, three kinds of zeolites with and without NiW sulfide are tested. Through the detailed analysis of the product distribution, the favorable acid properties for both reactions are discussed. In addition, the role of the hydrogenation active species in each reaction is compared.

2. Experimental

2.1. Catalysts

Three kinds of zeolites, USY, HY and mordenite (MORD), used in the present study were commercially available products. Each powder zeolite was sieved and the fraction between 75–250 μm was used for the catalyst preparation. The loading of NiW ($NiO=3.5$ wt%, $WO_3=24.0$ wt%) was performed by the incipient wetness method using an mixed solution of $Ni(NO_3)\cdot 6H_2O$ and $(NH_4)_6[H_2W_{12}O_{40}]$. After impregnation, the catalysts were dried at 383 K for 12 h in air, followed by calcination at 773 K for 3 h. As a reference which does not possess bifunctionality, an Al_2O_3 supported NiW catalyst with the same Ni and W loading was prepared. All the NiW supported catalysts were sulfided at 673 K for 2 h in a 5% H_2S/H_2 stream under atmospheric pressure prior to the model reactions and the below mentioned characterizations. The physical properties of the catalysts were measured by N_2 adsorption using a Micromeritics ASAP 2010 system. The acid strength distributions of the catalysts were measured by NH_3 temperature programmed desorption (NH_3-TPD). The chemical and physical properties of the catalysts with and without NiW are summarized in Table 1.

2.2. Model reaction

Diphenylmethane (DPM) and tetralin used in the present study were commercially available reagents without further purification. Hydrocracking reactions were performed using a 50 ml micro batch-type reactor with an electric furnace and a rocking system. The experimental conditions were as follows: model compounds; 3–5 ml, catalyst; 0.3 g, initial hydrogen pres-

Table 1
List of zeolite catalysts

Catalyst	BET surface area (m^2/g)	*t*-Plot external surface area (m^2/g)	Mesopore volume (ml/g)[a]	Acidity (mmol/g)[b]			Na content (wt%)
				Total	Weak	Strong	
USY (8.4[c])	621.3	75.0	0.145	1.01	0.55	0.46	0.13
NiW/USY	453.1	63.6	0.065	1.11	0.56	0.55	
HY (4.2[c])	650.5	71.7	0.114	0.77	0.63	0.14	2.96
NiW/HY	453.7	50.2	0.062	0.86	0.64	0.22	
MORD (7.9[d])	457.1	31.6	0.017	1.25	0.66	0.59	0.31
NiW/MORD	320.3	25.4	0.023	1.42	0.73	0.69	

[a] Mesopore ($17\ \text{Å}<D<3000\ \text{Å}$), calculated by the BJH method using the N_2 desorption isotherm.

[b] Estimated by NH_3-TPD. Weak acidity: amount desorbed at 423–623 K. Strong acidity: amount desorbed at 623–973 K.

[c] Si/Al ratio of zeolite framework calculated from the unit cell dimension using Breck's equation.

[d] Si/Al ratio measured by ICP.

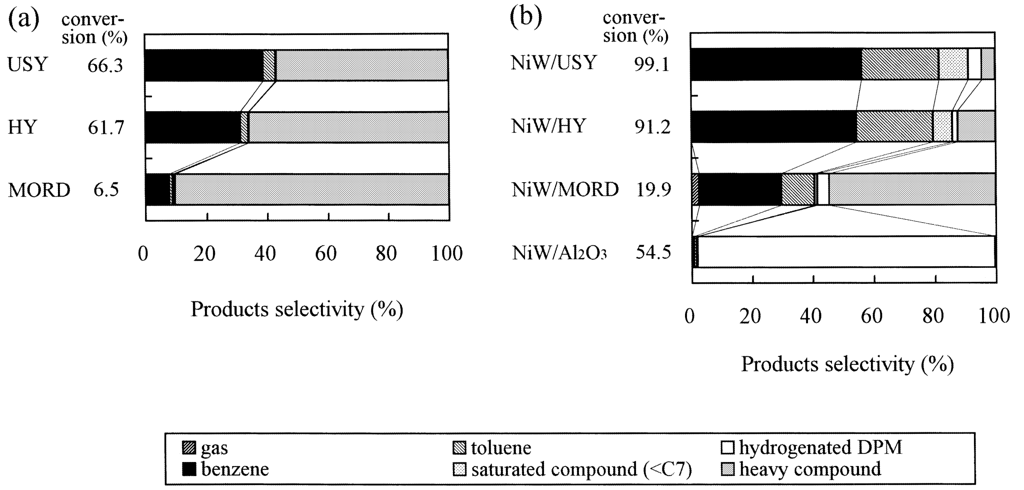

Fig. 1. Conversion and product distribution in DPM hydrocracking reaction over zeolite (a), NiW/zeolite (b). Reaction temperature: 623 K, reaction time: 1 h, catalyst weight: 0.3 g, DPM: 5 ml, initial H_2 pressure: 6.1 MPa.

sure; 6.1 MPa (cold charge), reaction temperature; 623 K, reaction time; 0.5–3 h. Liquid products were identified and determined using gas chromatographs with a mass spectrometer (Hewlett-Packard 5970) and a FID detector (Hewlett-Packard 5880).

3. Results and discussion

3.1. Hydrocracking of diphenylmethane

Fig. 1 shows the conversion and product distribution of diphenylmethane (DPM) hydrocracking reactions. Among the zeolites without NiW, the DPM conversion decreased in the order of USY>HY>> MORD (Fig. 1(a)). The selectivity to benzene and toluene which were the hydrocracked compounds of DPM was 10–40%. Much smaller yields of toluene compared with benzene were due to the polymerization of benzyl cations during the reaction. In fact, the GC–MS analysis recorded heavy compounds with *M/e* numbers of 182 258 348 which likely corresponded to methyl DPM, benzyl DPM and di-benzyl DPM.

The loading of NiW sulfide increased the DPM conversion over all the zeolites. Among the zeolite catalysts with NiW sulfide, the order of the DPM conversion was the same as the order for the zeolite without NiW. An evident effect of the NiW loading on the product distribution was found in the increase in the yield of toluene and the decrease in the yield of heavy compounds. In addition, hydrogenated products, such as cyclohexylphenylmethane, and their hydrocracked compounds, such as cyclohexane, were obtained over all kinds of NiW/zeolites. Significant differences were observed in the product distribution among the catalysts. Over NiW/USY and NiW/HY, the total yield of benzene and toluene was almost 80% with low selectivity to heavy compounds. On the other hand, a small amount of gaseous products in addition to a large amount of heavy compounds were yielded over NiW/MORD. High DPM conversion was obtained over NiW/Al_2O_3. However, most of the products were hydrogenated DPM with production of very small amounts of benzene, toluene and heavy compounds. It was confirmed that thermal cracking without catalyst did not take place under the present conditions.

3.2. Hydrocracking of tetralin

In the hydrocracking of tetralin at 623 K over zeolite catalysts, more than 300 compounds were detected by gas chromatography analysis. After identification by GC–MASS analysis, these compounds were classified into the following groups; (i) alkane gas (<C5), (ii) benzene and alkylbenzene, (iii) mono-ring saturated hydrocarbon (alkylcyclohexane etc.), (iv) decalin, (v) decalin isomer (methylperhydroin-

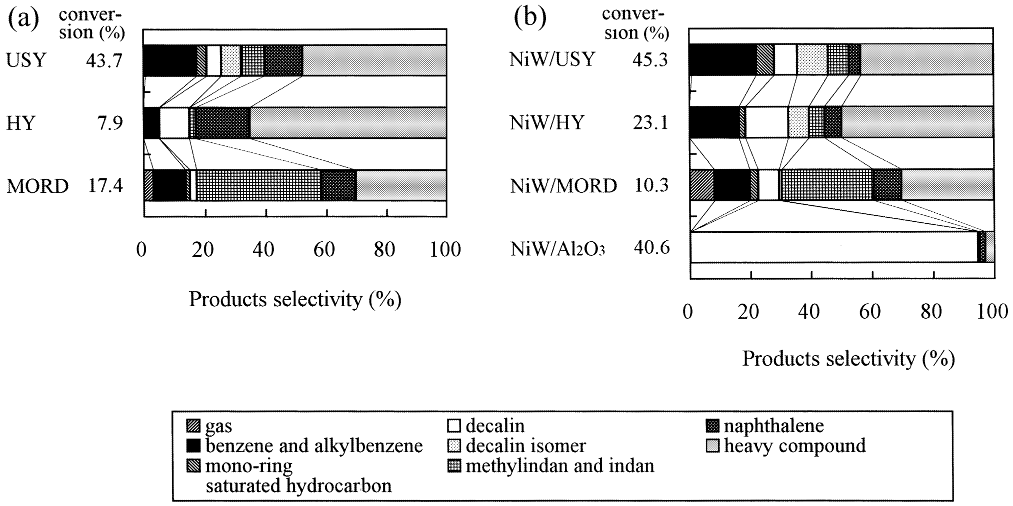

Fig. 2. Conversion and product distribution in tetralin hydrocracking reaction over zeolite (a), NiW/zeolite (b). Reaction temperature: 623 K, reaction time: 1 h, catalyst weight: 0.3 g, tetralin: 5 ml, initial H_2 pressure: 6.1 MPa.

dene etc.), (vi) indan and methylindan, (vii) naphthalene and (viii) heavy compounds (methyltetralin, oligomerized tetralin, hydrophenanthrene etc.). Fig. 2 shows the tetralin conversion and product distribution classified by this way.

Among the zeolites without NiW, the tetralin conversion decreased in the order of USY>MORD>HY (Fig. 2(a)). In contrast to the reaction of DPM, MORD showed high activity for tetralin. The product distribution greatly depended on the zeolite species. In particular, significant difference in the product distribution was observed between USY and MORD. USY exhibited the highest selectivity to hydrocracked products. In addition, relatively high selectivity to hydrogenated products and their isomers was obtained over USY. The product distribution over HY was analogous to that over USY, but the selectivity to hydrocracked products was much lower. On the other hand, MORD gave high selectivity to methylindan and gaseous products.

The tetralin conversion over NiW supported zeolite catalysts decreased in the order of USY>HY>MORD (Fig. 2(b)). The loading of NiW sulfide improved the conversion over HY, but did not significantly change the conversion over USY and decreased the conversion over MORD. The effect of the NiW sulfide loading on the product distribution was also different among the catalysts. In the case of USY, the selectivity to hydrocracked and hydrogenated products was slightly increased in parallel with the decrease in the naphthalene yield. The effect on HY was similar to that on USY. Over MORD, the selectivity to decalin and gaseous products was increased with keeping high selectivity to methylindan. The yields of heavy compounds were not significantly decreased by the loading of NiW sulfide over HY and USY zeolites.

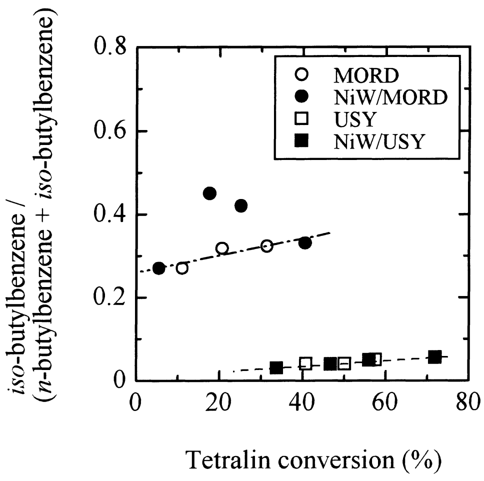

Fig. 3. Isomer ratio of buthylbenzene produced in tetralin hydrocracking. Reaction temperature: 623 K, reaction time: 0.5–3 h, catalyst: 0.3 g, tetralin: 3 ml, initial H_2 pressure: 6.1 MPa.

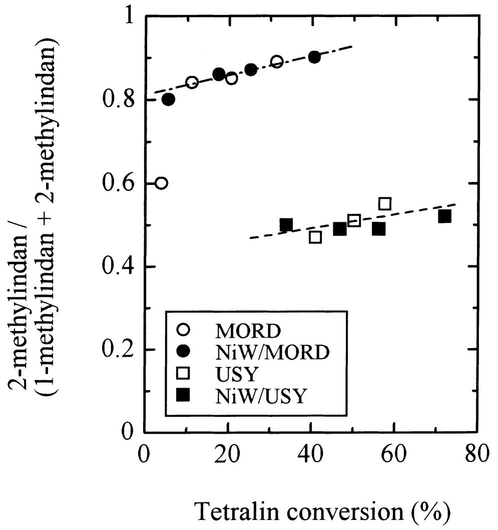

Fig. 4. Isomer ratio of methylindan produced in tetralin hydrocracking. Reaction temperature: 623 K, reaction time: 0.5–3 h, catalyst: 0.3 g, tetralin: 3 ml, initial H_2 pressure: 6.1 MPa.

Figs. 3 and 4 show the ratio of 2-methylindan relative to 1- and 2-methylindan and the ratio of iso-butylbenzene relative to *n*- and iso-butylbenzene, respectively. The selectivity to iso-butylbenzene was below 0.05 over USY, while 0.25–0.45 over MORD (Fig. 3). The selectivity to 1- and 2-methylindan was almost the same over USY, however, the selectivity to 2-methylindan was significantly higher than that to 1-methylindan over MORD (Fig. 4). These differences in the product distribution indicate the difference in the reaction path between USY and MORD.

The tetralin hydrocracking reaction network is illustrated in Fig. 5, which shows three major reaction paths for hydrocracking: (a) hydrogenation to decalin followed by ring-opening via methylperhydroindene, (b) direct ring-opening of tetralin, (b-1) to *n*-butylbenzene via 1-methylindan, (b-2) to iso-butylbenzene via 2-methylindan. Relatively high selectivity to decalin and mono-ring saturated hydrocarbons over USY indicates that the path (a) was catalyzed over USY. On the other hand, path (a) was very minor over MORD. Although USY gave almost the same selectivity to 1- and 2-methylindan, the yield of *n*-butylbenzene was much larger than that of iso-butylbenzene. This is due to higher stability of (I^*) cation than (II^*), which causes higher reaction rates for (b-1) than for (b-2). On the contrary, isomerization and stabilization to 2-methylindan from (I^+) via (II^+) is faster than the formation of (I^*) over MORD. Hence, the contribution

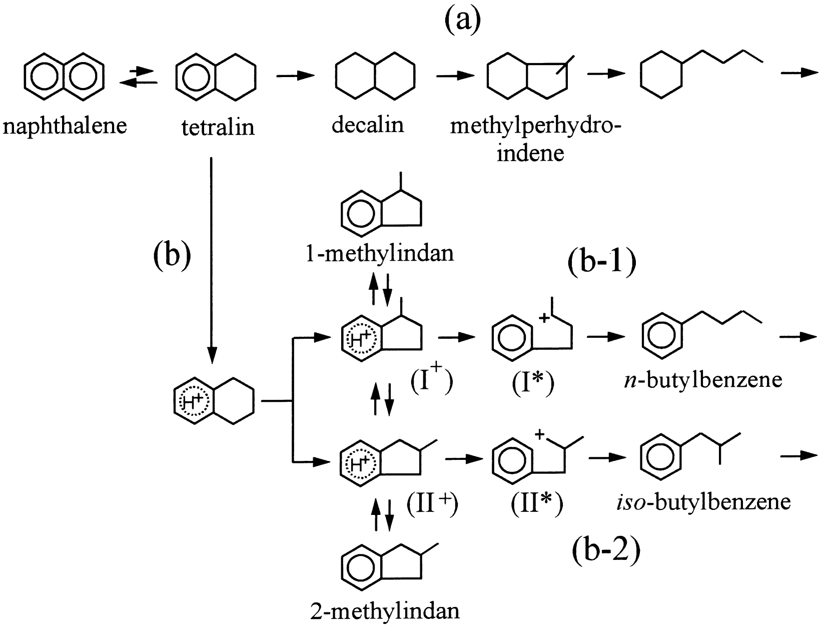

Fig. 5. Reaction network of tetralin hydrocracking.

of path (b-1) to the total hydrocracking reaction was relatively small over MORD. This resulted in the low selectivity to hydrocracked products over MORD in spite of the high yield of methylindan.

3.3. *Effect of zeolite properties*

The hydrocracking reactions described above are primarily related to the catalytic properties of zeolites. There are two possible factors which control the hydrocracking reactions over zeolites. One is diffusional limitation in micropores, which significantly suppresses the reaction of large molecules. The intrapore diffusional limitation of benzene, naphthalene and phenanthrene was negligible for faujasite or mordenite frameworks according to the CAMD simulation [4]. Although the difference in the micropore structures may not completely be neglected, we will focus on another factor here in after.

The other factor is the nature of solid acidity. The total amount of acid sites decreases in the order of MORD>USY>HY as shown in Table 1. MORD possesses the largest amount of strong acid sites. The order of the DPM conversion among the zeolites was not in agreement with that of the acidity. MORD exhibited low DPM conversion in spite of the large amount of strong acid sites. This suggests that strong acid sites are not needed for the DPM hydrocracking. The strong acid sites on MORD rather caused excess cracking leading to gaseous products. Thus, the acidic properties of MORD are not suitable for the DPM cracking.

On the other hand, somewhat strong acidity is needed for tetralin hydrocracking, since high conversion is achieved over USY and MORD without NiW sulfide. USY and HY showed similar activities for the DPM reaction, however, USY demonstrated much higher activity for the tetralin reaction than HY. This is most likely due to the high Si/Al ratio of USY, since other properties of USY are similar to those of HY as shown in Table 1.

Evident differences observed in the product distribution over USY and MORD are presumably due to the different acidic features between the two zeolites. Over both HY and USY, selectivity to hydrogenated products, such as decalin and its isomers, was quite high. Since Y-type zeolite does not possess hydrogen dissociation ability, the hydrogenation presumably takes place via inter-molecular hydrogen transfer. The decalin formation via path (a) in Fig. 5 proceeds by the hydrogen transfer between two tetralin molecules. In addition, the hydrogen transfer ability of zeolite probably enhances the formation of (I^*) in path (b), because the initial step of the C–C bond cleavage is dehydrogenation.

Corma and Orchilles [5] reported that the hydrogen transfer ability was influenced by the Si/Al ratio. The high Si/Al ratio of USY brings about high hydrogen transfer ability in addition to strong acidity. Both of the properties presumably play important roles in the hydrocracking of tetralin. The strong acid sites of MORD functioned for the conversion of tetralin. However, the acid sites catalyzed mainly isomerization leading to methylindan or excess cracking to gaseous products. This may be related to low hydrogen transfer ability of MORD as indicated in [6].

3.4. *Role of NiW sulfide supported on zeolite*

In the reaction of DPM, the selectivity to hydrogenated products was relatively low over the zeolites with NiW sulfide. Evidently, the function of NiW sulfide supported on the zeolite is different from that on Al_2O_3 which hydrogenates aromatic rings. As shown in the large increase in the toluene selectivity and the decrease in the heavy compound selectivity, the role of NiW sulfide on the zeolites is to supply the dissociatively adsorbed hydrogen to hydrocracking active sites on zeolite and to prevent the polymerization of the active cations. This function of NiW sulfide also resulted in the increase of the DPM conversion. Hence, the balance between the acidity and ability for supplying the dissociated hydrogen is an important factor for the hydrocracking of DPM.

The role of NiW sulfide in the tetralin hydrocracking is significantly different from that in the hydrocracking of DPM. NiW sulfide did not function for the prevention of heavy compound production from tetralin. Instead, the loading of NiW sulfide functioned for the hydrogenation of aromatic compounds, as shown in the increase in the hydrogenated products and the decrease in the dehydrogenated products. This resulted in the increase of the selectivity to hydrocracked products over all zeolites.

The effect of NiW sulfide in the tetralin hydrocracking was different among each zeolite. NH_3-TPD indicated that the amounts of strong acid sites were increased by the NiW loading over all zeolites. Binary sulfide systems are known to exhibit Brønsted acidity with the incorporation of H_2S [7], however, this does not result in strong acidity. In fact, NiW/Al_2O_3 did not catalyze hydrocracking of tetralin. The increased conversion of tetralin over HY by the loading of NiW sulfide are very likely attributed to the acid sites formed by the combination of zeolite and NiW sulfide. The increase in the tetralin conversion by NiW loading was not clearly observed over USY and MORD. The formation of acid sites associated with NiW sulfide may be dependent on the zeolite species.

Another factor controlling the effect of NiW sulfide may be the physical properties of the zeolite. The obvious feature of MORD is found in the extremely small mesopore volume compared with other zeolites (Table 1). For the other zeolites, the loading of NiW sulfide caused decreases in the mesopore volume, indicative of the occupation of NiW sulfide in the mesopores. Whereas, NiW sulfide was probably deposited on the external surface of MORD. The interaction between zeolite and NiW sulfide may be different between MORD and other zeolites. This may be a reason for the decrease in the tetralin conversion by the NiW sulfide loading over MORD.

The influence of coke deposition on the catalytic activities is sometimes critical in the reactions over solid acid catalysts. In fact, coke deposition was observed on all the zeolite-based catalysts in the present study. However, evident catalyst deactivation was not observed even when the reaction time was extended up to 3 h. This indicates that the effect of catalyst deactivation in the reaction results is relatively small within the present reaction conditions.

The NiW sulfide loading does not likely suppress the coke formation on the catalyst in the tetralin reaction, as evidenced by the little effect on the production of heavy compounds. In this respect, the mechanism of heavy compounds formation from tetralin over bifunctional catalysts should be elucidated.

Heavy oil contains various kinds of hydrocarbon structures. The present study has indicated that the roles of bifunctionality in hydrocracking reactions depend on the hydrocarbon structures. To design better hydrocracking catalysts, it is essential to understand precise molecular structures of feedstocks. In this regard, the study on the hydrocracking catalysts should be linked to the study on the first-stage hydrotreating. In addition, it will be important to develop solid acid supports with appropriate properties for hydrocracking and to elucidate proper combination of hydrogenation and hydrocracking active species.

4. Conclusion

The present study has discussed the effects of the zeolite properties and the roles of NiW sulfide in the hydrocracking reactions of DPM and tetralin. Summarizing the discussion, the following conclusions are obtained.

Strong acidity is not necessary for the hydrocracking of DPM, while the ring opening of tetralin needs relatively strong acid sites. Comparing the two zeolites with strong acidity, the acid sites of USY function for hydrocracking of tetralin, whereas those of MORD catalyze isomerization or excess cracking to gaseous products. The high hydrocracking activity of USY may be related to the hydrogen transfer ability of USY.

The roles of NiW sulfide are quite dependent on the structure of hydrocarbon and the supported zeolite species. In the hydrocracking of DPM, the major role is the supply of dissociatively adsorbed hydrogen to the hydrocracking active sites, which prevents the polymerization of benzyl cations. In the tetralin hydrocracking, NiW does not function for the prevention of polymerization but hydrogenates aromatic compounds which are yielded by the dehydrogenation of tetralin.

Acknowledgements

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