

CATALYSIS OF METAL-ION EXCHANGED Y-ZEOLITES AND MODIFIED Ni-Mo/Al₂O₃ FOR HYDROCRACKING OF PHENANTHRENE AND COAL-DERIVED DISTILLATES

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INTRODUCTION

The liquids derived from liquefaction, pyrolysis and gasification of coals have high contents of condensed polyaromatic compounds and polar compounds. Even in the middle distillate fraction (MD) produced from the advanced two-stage coal liquefaction plant at Wilsonville, Alabama, there are considerable amounts of polyaromatics such as pyrene [1]. These liquids require catalytic hydroprocessing before they can be used as clean transportation fuels such as gasoline and jet fuels. During the last two decades, emphasis in selecting catalysts for coal liquids upgrading has always been given to the Ni-Mo and Co-Mo combinations, which are used extensively in the petroleum industry. Research has focused mainly on catalyst screening and evaluation, and little attention has been given to investigating novel formulations [2].

In regard to catalytic materials, the use of zeolites is of both fundamental and practical importance because of their higher surface area and unique catalytic property as compared to conventional catalysts supported on alumina or silica-alumina. There are numerous reports on the application of various zeolites in the catalytic reaction processes related to petroleum industry [3-4]. Introducing transition metals into zeolites by appropriate methods could make the zeolite suitable for hydrocracking, and the metals can also serve to hydrogenate the coke precursors rapidly and to prevent their conversion to coke deposit on the zeolite [3]. There are also commercial hydrocracking processes using zeolite-based catalysts for converting petroleum distillates [3], and more recently, for converting residues [5-6]. However, the research work on zeolite catalysts in hydrocracking of polyaromatics and coal liquids is still very limited. Haynes et al. [7] studied hydrocracking of prehydrogenated polycyclic hydrocarbons over Ni-W impregnated on a Y-zeolite. They showed that mixtures of hydrogenated pyrenes can be hydrocracked over Ni-W/Y catalyst. Kikuchi et al. [8] studied hydrocracking of phenanthrene using LaY catalyst in the presence of H-donor tetralin solvent. They showed that this catalyst can significantly promote phenanthrene conversion if tetralin was present, otherwise Ni-Mo/Al₂O₃ was much more active than LaY. Our preliminary work has shown that some transition metal-ion exchanged Y-zeolites show some unique catalytic activity for hydrocracking of polyaromatics [9-10] as compared to other catalysts [10-12]. The work reported here aimed at clarifying the effects of loading small amounts of metals on the catalytic activity of Y-zeolite. In this work, we prepared several metal-loaded Y-zeolites by ion-exchange and evaluated the effects of these zeolite catalysts and of two third-generation commercial Ni-Mo catalysts in hydrocracking of phenanthrene, which is a typical polyaromatic component in liquids from pyrolysis and liquefaction of coals. Some of the catalysts were further examined in hydrocracking of a coal-derived middle distillate fraction which is rich in polyaromatics.

EXPERIMENTAL

The metal-ion exchanged Y-zeolites were prepared by mixing ammonium-exchanged Y-zeolite, NH₄-Y (SiO₂/Al₂O₃ mol ratio: 4.6) and 0.25 M aqueous solutions of Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, or La(NO₃)₃·6H₂O. The mixtures were agitated at 85°C for 2 h and then filtered. The ion-exchanged zeolites were washed with distilled water, dried at 120°C for 2 h and then calcined in air at 500°C for 4 h. Two commercial Ni-Mo catalysts were sulfided with 6% CS₂ in n-dodecane at 250°C for 2 h and 300°C for 3 h under 100 psi H₂, and used in phenanthrene hydrocracking. The chemical composition of both the metal-ion exchanged zeolites and supported Ni-Mo or Co-Mo catalysts was determined by inductively coupled plasma - atomic emission spectrometry (ICP-AES, Seiko Denshi Kogyo, JY-48P-SPS1100). The surface analyses of the zeolite catalysts, unsulfided and sulfided Ni-Mo catalysts were also conducted by X-ray photoelectron spectroscopy (XPS; Shimadzu ESCA-850, MgKα) and scanning electron microscope - electron probe microanalysis (SEM-EPMA; Nihon Denshi, JXA-733).

Hydrocracking of phenanthrene was carried out at 400°C for 1 h with 1000 psi H₂ (cold) in a 100 ml autoclave with phenanthrene (4 g), n-heptane solvent (10 ml) and a catalyst (2 g). The gaseous products were analyzed by GC. The liquid and solid products were analyzed by capillary GC-MS (Shimadzu QP-1000) and capillary GC (Shimadzu 9A). The used catalysts were washed by methylene chloride solvent, dried in vacuum oven at 100°C, and analyzed for carbonaceous deposits by combustion method.

We also used a coal-derived distillate sample (b.p. 204-343°C), which was produced from two-stage liquefaction of Ireland Mine coal at Wilsonville two-stage liquefaction plant using Shell 324 Ni-Mo catalyst [1]. Hydrocracking of Wilsonville middle distillates (WI-MD) was carried out at 400°C for 1 h with 1500 psi H₂ (cold) in 20 ml microautoclaves with 2 g feedstock and 0.4 g catalyst. The zeolite catalysts (NiH-Y, FeH-Y) were exposed to the feedstock in the microautoclave for about 20 hours before the reaction. The gas products were analyzed by GC. The liquid products were characterized by capillary GC-MS using a Kratos MS80 GC-MS system.

RESULTS AND DISCUSSION

Catalyst Characterization

In general, the extent of metal-ion exchange depends on the conditions and the samples used. In this work, the contents of metals of the prepared catalysts, and the change in chemical composition of the Y-zeolite framework before and after the metal-ion exchange were determined by using the ICP-AES technique. As shown in Table 1, the introduction of Ni, Fe and La into the NH₄-Y zeolite by ion-exchange was successful and the contents of these three metals in the finished catalysts are 3.6 (NiO), 4.4 (Fe₂O₃) and 8.4 (La₂O₃) wt%, respectively. For NiH-Y and LaH-Y catalysts, the SiO₂/Al₂O₃ ratios of the zeolites are similar to the original NH₄-Y or H-Y. However, in the case of FeH-Y, the content of Al₂O₃ is significantly less and the SiO₂/Al₂O₃ ratio is substantially higher than the other two catalysts. This indicates that the preparation of FeH-Y was accompanied by remarkable dealumination from zeolite framework, probably due to the higher acidity of the aqueous solution with Fe(NO₃)₃·9H₂O and NH₄-Y. In fact, we measured the pH of the aqueous solutions of the Fe, Ni and La salts before ion exchange, which were 1.1, 3.5, and 4.2, respectively. It is known that steam or acid treatment can cause dealumination of Y-zeolite [13].

SEM indicated that the size and shape of the three metal-ion exchanged zeolites are very similar to that of H-Y (un-exchanged). XPS spectra of NiH-Y and FeH-Y clearly showed a strong signal of Ni and Fe on the zeolite surface. The binding energies for Al 2p or Si 2p of NiH-Y and LaH-Y are similar, while the intensity of Al 2p for FeH-Y is very low (with high noise signals), 72 cps as compared to 730 cps for Al in NiH-Y and 636 cps for Al in LaH-Y. This is considered to be due to the very low content of Al in FeH-Y, being consistent with the finding from ICP-AES. Surprisingly, ICP-AES indicated that LaH-Y contains 8.4 wt% La₂O₃, but XPS showed that the intensity of La on the surface is very low. However, it was found that when the etching technique was applied in XPS (for the depth distribution from surface to the bulk), the intensity of the peak of La increased remarkably with increasing etching time from 0.4 to 1.2 min, whereas there was little change in the relative intensity of peaks for Al and Si in LaH-Y with etching from 0 to 1.2 min. These results clearly indicate that the concentration of La in the bulk or framework is higher than that on the zeolite surface. We also examined two alumina-supported NiMo catalysts obtained from two catalyst companies, which are currently being used in many commercial plants for hydroprocessing of petroleum feedstocks. Detailed analyses by ICP-AES, SEM-EDPA and other techniques revealed that one of the third-generation NiMo catalysts contains P, and the other contains B. It is clear from the figures in Table 1 that B or P was intentionally added to improve the catalyst property or performance. XPS analysis showed that spectra pattern of the Mo 3d doublets of the two catalysts is similar to each other, but the Ni 2p peak for the P-modified NiMo is relatively sharper, suggesting a better dispersion of Ni.

Phenanthrene Hydrocracking

In this work, we examined the catalytic effects of the metal-ion modified Y-zeolites (NiH-Y, FeH-Y, LaH-Y) and H-Y for hydrocracking of phenanthrene. The catalytic activity of these zeolites was also evaluated by comparing with two commercial Ni-Mo catalysts. Numerous products were formed during the catalytic hydrocracking of phenanthrene. These products can be classified into the following groups: 1) C₁-C₄

gases; 2) C5-C7 aliphatics; 3) alkylbenzenes; 4) alkyltetralins and alkylindans; 5) alkylnaphthalenes; 6) alkylbiphenyls; 7) unsym-octahydrophenanthrene and octahydrophenanthrene isomers; 8) sym-octahydrophenanthrene; 9) methylbenzoindans; 10) tetrahydrophenanthrene; 11) dihydrophenanthrene; 12) phenanthrene; 13) alkylphenanthrenes; 14) carbonaceous deposits; and the others. Figure 1 shows some typical results of GC-MS and GC analysis of products from hydrocracking of phenanthrene with different catalysts. Table 2 is a summary of the results with all the catalysts. As can be seen from Figure 1 and Table 2, the product distribution and phenanthrene conversion strongly depend on the metal introduced into the Y-zeolites. When H-Y is used, alkylbenzenes and alkylnaphthalenes were obtained as major hydrocracked products together with C1-C4 gases. The La-exchanged zeolite, LaH-Y (Figure 1B), gave similar results to those with H-Y. Yields of alkyltetralins were very low but more than 10wt% of methyl and dimethylphenanthrene were formed with LaH-Y and H-Y, probably due to transalkylation between alkylnaphthalenes or alkylbenzenes and phenanthrene. Interestingly, introducing Ni to Y-zeolite significantly promoted the hydrocracking activity, as can be seen from comparison of Figures 1A with 1B. In fact, NiH-Y afforded much higher conversion and higher yields of BTX, especially toluene. Moreover, not only alkylnaphthalene but also tetralin and methylindanes were obtained as two-ring hydrocracked products with NiH-Y. On the other hand, FeH-Y showed quite a different catalytic behavior as compared to H-Y, NiH-Y and LaH-Y. While naphthalene was also produced with FeH-Y, the major products are dihydro- and tetrahydro-phenanthrene. The formation of alkylphenanthrenes and carbonaceous deposits was suppressed significantly with FeH-Y. These results indicate that FeH-Y has a very low acidity as compared to the other zeolites, probably due mainly to the dealumination as revealed by ICP-AES. The runs over supported Ni-Mo catalysts afforded partially hydrogenated phenanthrene as main products (Figure 1 and Table 2), and the major cracking products are alkyltetralins, cyclohexylphenylethane, cyclohexylbenzene, and alkylbiphenyls together with small amounts of alkylnaphthalenes. While the two catalysts from different sources have different metal contents, it appears that the P-modified catalyst shows higher hydrogenation activity than the B-modified one but the latter has a relatively higher cracking ability than the former (Table 2). We have observed a similar trend for P- and B-modified Co-Mo/Al₂O₃ catalysts [9-10]. Comparison of Figure 1A with Figure 1C reveals that NiH-Y has much higher hydrocracking activity than the industrial Ni-Mo hydroprocessing catalyst.

The differences in product distribution also reflect the occurrence of different reaction paths. It is worthwhile noting from Figure 1 and Table 2 that yields of alkylbiphenyls are considerably lower with the Y-zeolite catalysts, probably because the ring-opening cracking of dihydrophenanthrene is difficult with the catalysts having strong acidity, such as H-Y, NiH-Y and LaH-Y. This consideration is also supported by the fact that considerable amounts of biphenyl and cyclohexylbenzene were formed with the relatively less acidic Ni-Mo/Al₂O₃ (Figure 1, Table 2), probably via the hydrocracking of the central ring in 9,10-dihydrophenanthrene. The relatively higher yields of alkylnaphthalenes with LaH-Y and H-Y suggests a major hydrocracking path via tetrahydrophenanthrene, whereas the higher yields of alkyltetralins and cyclohexylphenylethane (Figure 1) with the Ni-Mo catalysts implicate the paths of hydrocracking via sym- and unsym-octahydrophenanthrene. It seems that both these two paths exist for the hydrocracking with NiH-Y catalyst, probably because it has both high acidic cracking ability and high hydrogenation activity. Since the critical diameter of phenanthrene is 7.9 Å [7] which is similar to the diameter of Y-zeolite (about 8 Å), the hydrocracking reactions with H-Y may have been associated mainly with the external surface of the zeolite. The metal-ion exchange may induce some dealumination, which could generate some mesopores in the zeolite [6]. ICP-AES clearly indicated the dealumination during the preparation of FeH-Y. At the present stage, it is not clear whether this occurred during the preparation of NiH-Y and LaH-Y, but the "apparent" SiO₂/Al₂O₃ ratios of these two zeolites are similar to that of H-Y.

Hydrocracking of Wilsonville Middle Distillates

From the above results, it is clear that the zeolite ion-exchanged with Ni or Fe exhibits distinctly different catalytic activity as compared to LaH-Y and H-Y. We further examined NiH-Y and FeH-Y for hydrocracking of WI-MD, which has a boiling range of 204-343°C. Because it was produced from direct liquefaction of coal and because of the co-boiling phenomena, it has high contents of polyaromatic materials [1]. The hydrocracking of WI-MD was conducted at 400°C with 1500 psi H₂. In order to derive useful data on the applicability of the zeolitic catalysts for converting WI-MD, the FeH-Y and NiH-Y were immersed in the WI-

MD for over 20 hours before the reaction. This was intended to deactivate the active sites in the zeolite catalysts which would be poisoned upon contact with coal-derived distillates in a continuous reactor. In this way we might be able to see the activity level of the active sites which are not poisoned by the adsorption of polar and polyaromatic materials. Figure 2 shows the GC-MS total ion chromatograms of the liquids from a non-catalytic run and catalytic runs. The GC-MS profile of the liquids from a noncatalytic run of WI-MD (Figure 2A) is very similar to the original sample [1]. Both samples contain very limited amounts of aliphatics, and are rich in polyaromatics. The most predominant peak appeared in GC-MS total ion chromatogram in Figure 2A (scan No. 3683, retention time: 59:31 min) is pyrene. The use of FeH-Y, after its 20 h exposure to WI-MD prior to reaction, did not alter the liquid composition to any significant extent. On the other hand, using NiH-Y catalyst significantly promoted the hydrocracking reactions, and resulted in a dramatical change in the composition of liquid products. The major products identified by GC-MS include alkylcyclohexanes, alkylbenzenes, tetralin and naphthalene and their homologues.

CONCLUSIONS

In summary, it has been found that NiH-Y, the proton form Y-zeolite loaded with Ni by ion exchange, shows much higher activity for phenanthrene hydrocracking than LaH-Y, H-Y, FeH-Y and commercial, B- or P-modified NiMo/Al₂O₃ hydroprocessing catalysts. The test with WI-MD also revealed that NiH-Y has high hydrocracking activity for converting the middle distillates derived from direct coal liquefaction. While some problems such as coking and pore size limitations remain to be solved, the preliminary results showed that some metal-ion exchanged zeolites can be promising hydrocracking catalysts. In future we hope to explore novel zeolitic catalysts with desired activity and performance for converting coal-derived distillates into transportation fuels.

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Table 1. Chemical Composition of the Metal-Ion Exchanged Y-zeolites and Supported Ni-Mo/Al₂O₃ Catalysts Determined by ICP-AES

| wt%, dry | NH ₄ -Y | H-Y | NiH-Y | FeH-Y | LaH-Y | P-Modified NiMo/Al ₂ O ₃ | B-Modified NiMo/Al ₂ O ₃ |
|--|--------------------|------|-------|-------|-------|---|---|
| NiO | | | 3.6 | | | 3.7 | 2.4 |
| Fe ₂ O ₃ | | | | 4.4 | | | |
| La ₂ O ₃ | | | | | 8.4 | | |
| MoO ₃ | | | | | | 18.5 | 9.2 |
| SiO ₂ | 71.6 | 73.3 | 70.6 | 91.5 | 66.5 | | |
| Al ₂ O ₃ | 26.7 | 26.2 | 25.5 | 2.2 | 24.7 | 68.2 | 71.8 |
| Na ₂ O | 0.9 | 0.4 | 0.3 | 0.1 | 0.3 | | |
| P ₂ O ₅ | | | | | | 7.8 | |
| B ₂ O ₃ | | | | | | | 12.2 |
| SiO ₂ /Al ₂ O ₃ | 4.55 | 4.76 | 4.70 | 69.46 | 4.56 | | |
| SA, m ² /g | 719 | 646 | 665 | 342 | 662 | 162 | 268 |

Table 2. Results of Catalytic Hydrocracking of Phenanthrene at 400°C with 6.9 MPa H₂

| Catalyst | H-Y | NiH-Y | FeH-Y | LaH-Y | S-NiMo/ Al ₂ O ₃ -B ₂ O ₃ | S-NiMo/ Al ₂ O ₃ -P ₂ O ₅ |
|--|------|-------|-------|-------|--|--|
| Products ^{a)} (wt%) | | | | | | |
| C ₁ -C ₄ | 2.4 | 8.5 | 0.2 | 2.2 | 0.5 | 0.4 |
| C ₅ -C ₇ | 0.4 | 0.4 | tr. | 0.6 | 0.2 | tr. |
| R ₁ -  -R ₂ ^{b)} | 1.0 | 6.9 | 0.1 | 1.4 | 1.5 | 1.7 |
| R ₁ -  -R ₂ | 0.7 | 4.4 | 0.2 | 0.7 | 4.4 | 3.3 |
| R ₁ -  -R ₂ | 4.4 | 6.3 | 1.0 | 3.8 | 1.8 | 0.8 |
|  -  -R | 0.2 | 0.4 | 0.1 | 0.1 | 1.3 | 1.8 |
|  ^{c)} +  -R | 0.7 | 2.9 | 0.2 | 1.4 | 8.1 | 9.0 |
|  ^{d)} | 0.5 | 2.4 | tr. | 0.5 | 6.2 | 11.8 |
|  -R ^{e)} | 2.0 | 3.6 | 0.7 | 1.9 | 1.9 | 1.0 |
|  | 1.3 | 2.7 | 4.6 | 1.2 | 16.7 | 17.0 |
|  | 1.8 | 2.4 | 6.2 | 1.9 | 7.6 | 10.1 |
|  | 53.3 | 19.3 | 80.4 | 54.0 | 31.6 | 30.5 |
| R ₁ -  -R ₂ | 11.2 | 8.7 | 1.1 | 10.3 | 1.0 | 0.4 |
| C deposits ^{f)} | 11.5 | 11.3 | 2.5 | 11.3 | 3.6 | 3.2 |
| Conversion (wt%) | 46.7 | 80.7 | 19.6 | 46.0 | 68.4 | 69.5 |

a) R, R₁ and R₂ mean alkyl groups or hydrogen. b) Including cyclohexyl phenylethane and cyclohexylbenzene. c) Unsym-octahydrophenanthrene. d) Sym-octahydrophenanthrene. e) Including some unknown components with molecular weight (by GC-MS) of 182. f) Amount of carbonaceous deposits on catalyst as determined by combustion method.

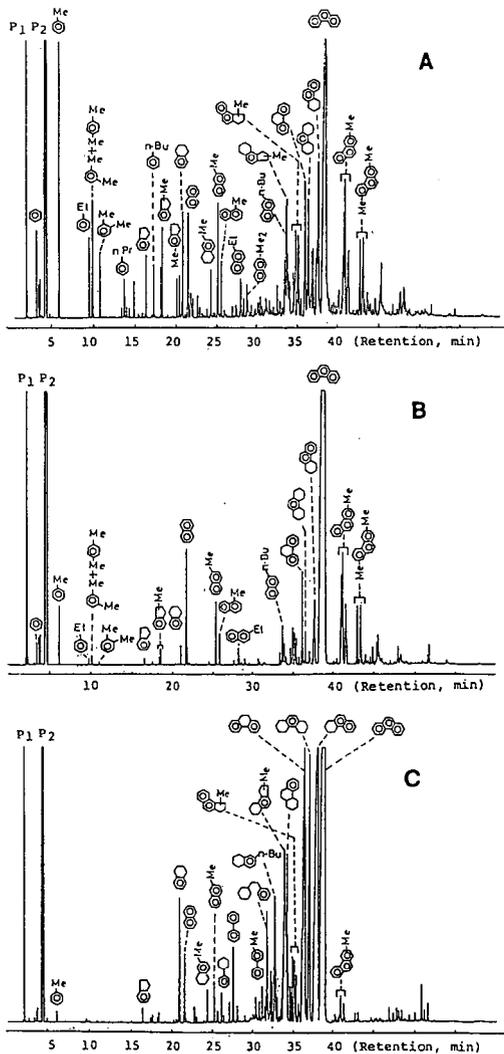


Figure 1. Composition of products from hydrocracking of phenanthrene over NiH-Y (A), LaH-Y (B) and commercial, B-modified NiMo/Al₂O₃ (C) catalysts (P₁: CH₂Cl₂ solvent; P₂: n-heptane solvent)

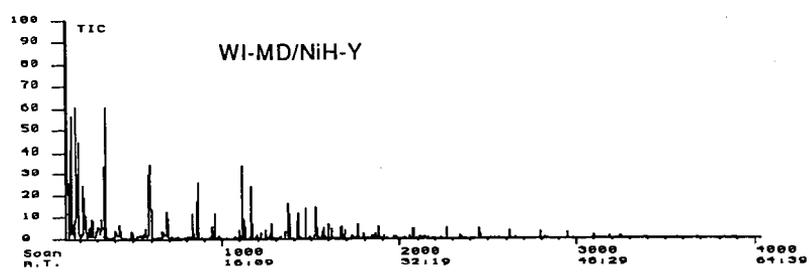
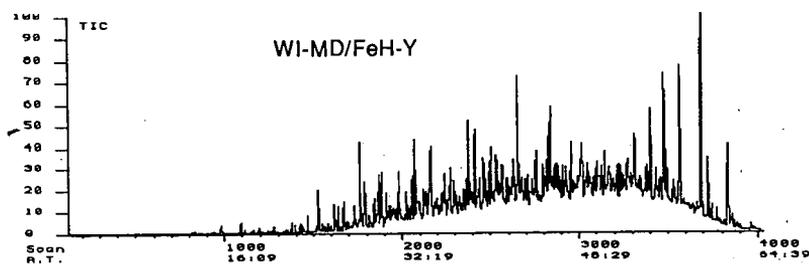
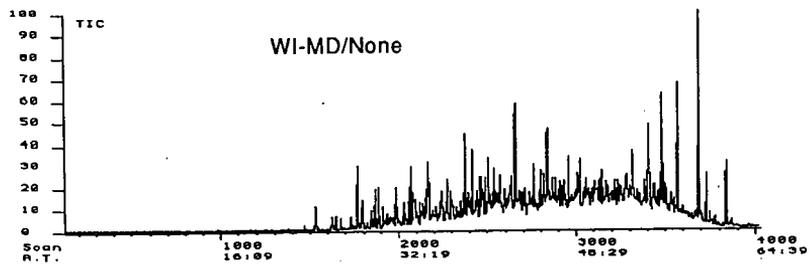


Figure 2. GC-MS TIC of liquid products from hydrocracking of Wilsonville middle distillates