Molecular and Molecular Assembling Approaches to Develop Efficient Catalytic Processes of Hydrocarbon Fuels

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Introduction

Hydrocarbon fuels are expected to play major roles to meet energy demands on the earth in the initial half of 21 century. Nevertheless, their efficient use and up-grading are strongly required to save the sources, and reduce environmental load. The up-graded products of the highest efficiency and least contaminants are designed through an adequate structural understanding of hydrocarbon fuels and their up-grading catalytic processes based on their structural information about the feeds, intermediates and products. Catalysts are the keys for up-grading processes. Designs of their adequate uses and materials for higher activity, selectivity and life are equally concerned.

Results and Discussion

Structural Understanding of Hydrocarbon Fuels and Molecular Understanding of Gasoline and Gas oils

Environmental regulation such S, N and aromatic contents as well as the combustion performance such as octane and cetane numbers require severer up-grading. The molecular basis reaction design which requires the reactivity of every constituents molecules is now studied by describing structure and contents of every molecules. GC-AED developed by Hewlett-Packard and Chevron is a powerful tool to analyze every molecules by classifying them according to their elemental composition detected by AED(atomic emission detector) after the separation by GC.

Figure 1 illustrates chromatograms of a gas oil by detecting C, S and N, respectively. Thus, the elemental composition of every species detected is obtained by this tool. By combining GC-MS to identify the molecular weight of the every peak, molecular composition of the peak is identified. There is, of course, limitation due to the chromatographic separation as shown in the N chromatogram where a broad hump is observed in a particular gas oil. The acid-extraction separates species in the hump from the other nitrogen species as basic nitrogen species, giving individual peaks to be identified as shown in Figure 2.

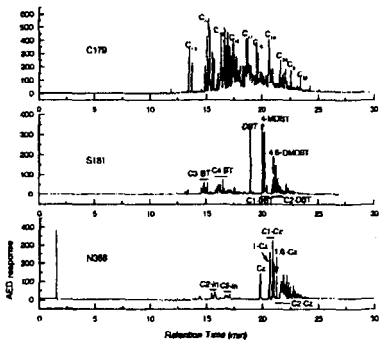


Figure 1. C, S and N chromatograms of MCO measured by GC-AED. C_n:normal paraffin with n number of C and C1~C4:1~4 substituted methyl groups.

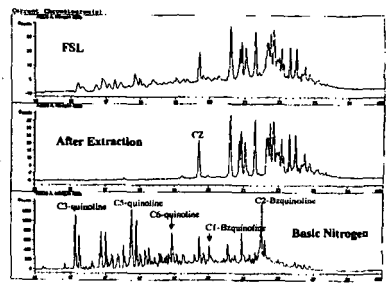


Figure 2. Basic fraction of FSL extracted by sulfuric acid. Background was successfully removed and it was analyzed as quinoline and benzoquinoline derivatives using GC-MS.

Approaching to Molecular Understanding of Vacuum Gas Oil

Vacuum gas oil is an important feed stock to be further up-grading rather easily by catalytic cracking through hydrodesulfurization/hydrodenitrogenation and hydrocracking. Their molecular identification has not been achieved yet by GC-AED. However, narrow cut distillation and selective separation(nitrogen by acid extraction and sulfur by PdCl chromatogram) are expected to separate it suitable for GC-AED analyses.

Molecular and Molecular Assembling Understanding of Resid and Coal

Resid and coal consist basically of polyaromatic-polynuclear macromolecules. The aromatic rings carry alkyl chains, being linked through methylene, aryl-aryl, ether, and thioether bonds. The aromatic ring carries also the heteroatoms within the ring. The sizes of molecules, aromatic ring and alkyl chains as well as the number of nuclei vary according to coals and crudes, although there are several trends which describe empirically such structural parameters.

Complex mixtures of molecular species in resid and coal carries parafins and naphthalenes of large molecular size. Such mixtures of macromolecules gather to form micelle or solid glass, through the intermolecular linkages. Hydrogen bonding, charge-transfer, alkyl entanglement and π-π ring stacking are proposed to exist. Figure 3 illustrates XRD profile of resid and coal. Definite diffractions are observed at around 20 and 26, which are ascribed to alkyl entanglement and π-π ring stacking.

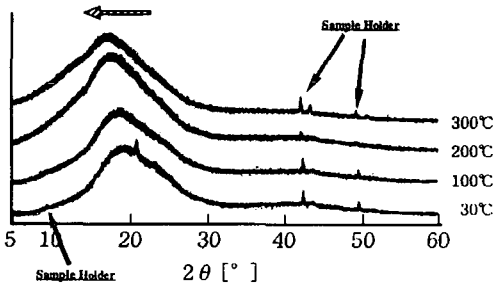


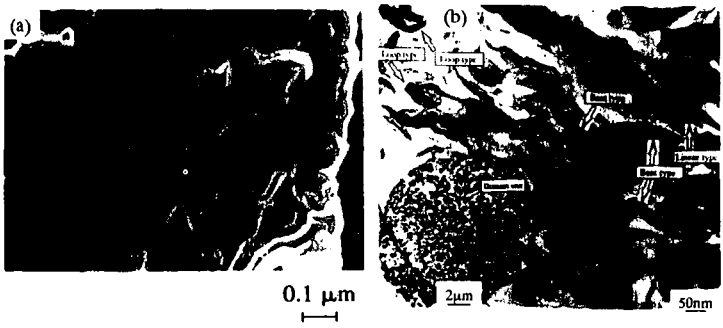
Figure 3. XRD of coal and resid (Measuring Temp. : 30~300°C, Step Scan : 4sec/0.01 °C, He atmosphere).

Resid and coal also carry same inorganic constituents. V=O and Ni porphyrins, minerals and ion-exchangeable cation are representative inorganic components in the former and latter fuels, respectively. Such inorganic constituents often provide bridges between macromolecules, or macromolecular chains.

Structure of Char

High molecular weight hydrocarbons tend to give char/coke when heated, liberating smaller molecules and cracked products. Such char/coke is a trouble maker as plugging and poisoning substances in the process, as well as combustible and gasifiable solid fuel. Their structure is also important to prevent their formation and to enhance the reactivity. Although the char/coke tends to carry some heteroatomic material when formed at lower temperature, it consists basically of hexagonal network. The size of hexagons and their stacking varied according to its experienced temperature, forming conditions and starting feed, approaching to the graphitic structure. Such microscopic stacking units gather to form micro domain, domain, and texture by orienting the microcrystallines and their assembles, respectively.

Recent development of high resolution SEM, TEM and STM/AFM in addition to XRD clarifies such micro, meso and macroscopic structure of char/coke. Figure 4 illustrates typical high resolution SEM, TEM and STM photographs of mesophase pitch based carbon fiber to show a series of structure.



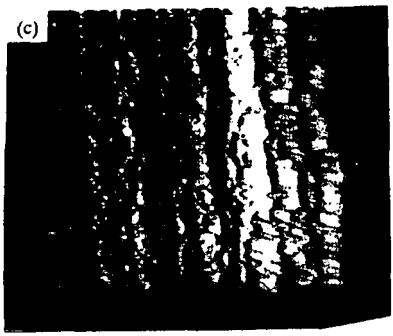


Figure 4. SEM, TEM and STM photographs of mesophase pitch based carbon fiber (a)HR-SEM photographs (outer section) (b)TEM BF images of the transverse section (total transverse image in the rectangular) (c)STM images of the longitudinal section.

Structural Understanding of Up-grading Schemes

Desulfurization and Denitrogenation of Gas Oil

The problem in the deep desulfurization of gas oil has been identified as the low reactivity of 4 and 6 alkyldibenzothiophenes. Their desulfurization has been proposed to proceed through hydrogenation of outer phenyl ring prior to the desulfurization at the relatively lower temperatures and direct desulfurization as another major desulfurization route at relatively higher temperatures.

GC-AED can follow the schemes of the substituents among other thousands of coexisting partners in the real feed which are strongly influenced by the coexisting partners as well as the catalyst performances. The former influences are defined as inhibitions which often restrict the deep desulfurization of the targeted level. Nitrogen and aromatic species, H_2S and NH_3 and their products are major inhibitors, their inhibiting factors being quantified to design the reactor, the process, and the catalyst. It is to be noted that the inhibitors are reactive to change their forms, strengthening or weakening the inhibition. GC-AED can also follow such change of structure and inhibitors at the same time.

Denitrogenation is also a target of refining. Reactivity, inhibition and susceptibility to inhibition of other nitrogen species are studied similarly. Figure 5 illustrates the reactivity of nitrogen species and the changes of their forms during the reaction, conforming the reaction scheme.

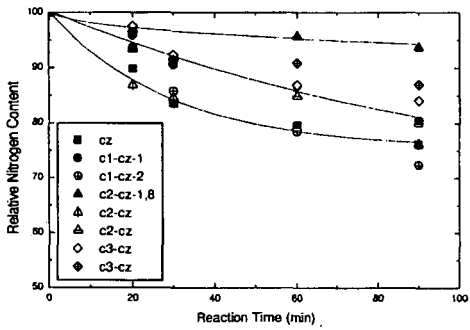


Figure 5. Reactivity of nitrogen species in FSL hydrotreated over $NiMo/Al_2O_3$ catalyst at 340 °C under 5Mpa of H_2. Background is removed in calculation. Number before and after symbol means number of methyl group and its location.

Desulfurization and Hydrocracking of Vacuum Residue and Coal Liquefaction

Longer term operation and higher middle distrate yield have been continually pursued in the desulfurization of vacuum residue. The reactivity of asphaltene for coking or strong adsorption as well as cracking, hydrogenation, desulfurization and removal of metals in asphaltene are major concerns. The higher conversion of asphaltene is a key to improve the efficiency in the coal liquefaction.

Changes of polymeric structure in the reaction suggest the route of distillate production. GC-AED is a powerful tool to identify the cracked products as the elemental parts of asphaltene.

Changes of asphatene tell us schemes for dry-sludge and coke/carbon formation. The authors are interested in clarifying by XRD the change in the entanglement and stretching of the asphaltene in the heated solvent through the hydrogenation, cracking, and dealkylation.

Reactivity of Char for Gasification

The reactivity of char, coke/coal or the graphite has been major research interest. However severer conditions in terms of temperature rather than the reaction, non-catalytic process and gasifying reagent appear to suggest that the reactivity is basically governed by rather physical fractors to influence the reactivity for gasifying conditions. The gasification of the next generation may revive the catalytic one under mild conditions to produce products of higher calorific value. The reactivity to achieve complete conversion of carbon may reflect the chemical structure of the hexagons and their assembles. The contact or holding and transfer of the catalyst are the other concerns.

Catalyst and Process Designs of Hydrocarbon Fuel Up-Grading

Deep desulfurization

Gasoline and diesel fuel have been regulated to carry S contents less than 30 and 50 ppm, respectively by the year around 2005. Desulfurization has been a major target of petroleum refinery, and further revolutional reduction of S is now within the scope.

Process and catalyst designs are equally pursued. According to the references, how to enhance the reactivity of refractory sulfur species and to reduce the inhibition are keys for the design.

Multi-stage processes have been proposed for this purpose. Reduction of product inhibition, in addition to selective activation of refractory sulfur species and suppression of partner's inhibition, is a key issue for the process. The author proposed a reactor of a novel concept as shown in Figure 6. There are problems to be solved in the catalyst form. Nevertheless, I believe it is possible and useful.

The removal of trace refractory species is another way to achieve deep desulfurization. The regeneration of remover and use of removed species are the tasks to be solved. Carbon with catalytic function can be a promising candidate for this purpose.

The catalyst for deep desulfurization has been continuously looked for. Higher activity of alumina supported sulfide has been achieved to satisfy the present regulation. Novel supports in addition to combinary sulfides can be targets to be studied. Acidity of the support is now concerned in the desulfurization in terms of hydrogenation, isomerization and resistivity against H_2S. Basic nitrogen species including NH_3 must be taken care of to reduce their inhibition and catalyst deactivation.

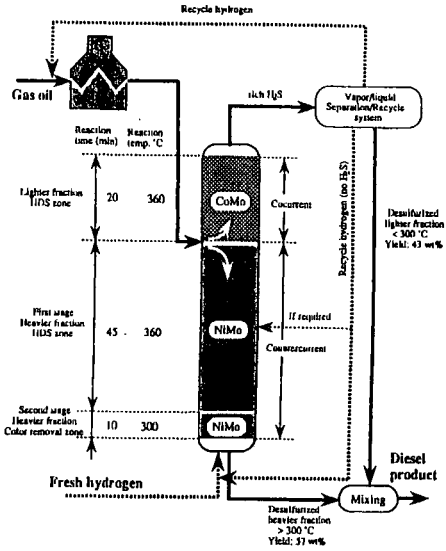


Figure 6. Deep HDS reactor design with cocurrent and countercurrent liquid-gas contact in separate catalyst beds.

Hydroprocessing of Vacuum Residues

Hydroprocessing of vacuum residue has been designed to consist of several steps, removal of solid contaminants such as NaCl and FeS, catalytic demetalation, catalytic modification of

heavy asphaltene and catalytic desulfurization of whole VR including asphaltene. Removal of solid contaminants is very important for the life of the catalytic reaction, because they are triggers of coke plugging in the guard and catalyst bed front although the step is often ignored. Soluble precursors of the iron often pass through the filter to deposit on the guard where FeS accelerates physically and chemically the coke formation.

Deep demetalation and capacity of the demetalation agent are most wanted to prolong the continuous operation time. Better demetalation agents are strongly wanted. Chevron patented a moving bed demetalation, enlarging the capacity by continuous feed of the agent. Pore size is considered very important to accept heavy asphaltene which carries most of prophyrins. Large surface area to fix the metal sulfides is also important for large capacity. Hence pore size and surface area are compromised.

HDS of asphaltene requires also enough size of pores to asphaltene. Thus, the digestion of asphaltene is key factor of the hydroprocessing and hence liberation of micelle is particularly important. Otherwise only maltene and light asphalene are hydrotreated, leaving heavy asphaltene unreacted or thermally dealkylated, resulting in the formation of dry sludge.

The author has proposed prehydrogenation of asphaltene at lower temperatures to break mineral, reducing the coking to enhance the demetalation and HDS. Nano-particle carbon composite can be a candidate for these purposes. Such carbons carrying NiMoS have been proved an excellent catalyst for coal liquefaction. Low gravity allows the recovery from ash minerals after the liquefaction.

Catalytic Gasification

The author believes that the catalytic gasification of new generation is in time of development after the slugging and fluidized bed gasification. The catalytic activity of highly dispersed catalytic materials on the char surface has been reported remarkably high through the spillover mechanism. The difficulty of the catalytic gasification is how to keep the intimate contact between the catalyst molecules and chars both of which are usually solid of certain particle size. Fluidized bed of char in the catalyst bed materials may realize such a catalytic gasification. However the contact of the catalyst particle and the char is limited only at their outest surface, catalytic efficiency becoming so low. The formation of sulfate, chloride or even carbonate deactivates the catalyst. The present authors have proposed a catalytic missile of alkali metal which can go back and forth between char surface and support. Perovskite type oxide has been proved to play such a role of support. Another important feature is to activate the inactive form of the metal salts by virtue of catalytic reduction with char on the support surface. Such a reduction allows the repeated travel between the char and support. The demonstration by the moving bed is now under planning.

Conclusions

Fuel science in 21 century must emphasize three aspects.

1. Very basic understanding and problem shooting of on-going fuel processing technology
2. Support to the developing processes in terms of smooth operation with lower cost and better efficiency
3. New concepts for fuel processes of the next generation

Fuel science can help or create the novel processes and essential trouble shorts based on the better understanding of fuels and their natures at their fundamental levels.

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Key words : hydrocarbon fuel, catalytic process, molecular approach.