An Integrated Approach to Utilization of Coal for Specialty Chemicals, Materials and Advanced Jet Fuels

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ABSTRACT
This paper will discuss an approach in research for more effective conversion and comprehensive (fuel and non-fuel) utilization of coal for making specialty organic chemicals, carbon-based materials and advanced thermally stable jet fuels. It also discusses shape-selective synthesis of specialty chemicals and polymer materials from coal-derived liquids.

1. INTRODUCTION

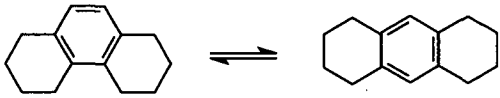
This article is a selective overview for recent research in our laboratory that was designed for more effective conversion and comprehensive utilization of coal for making specialty organic chemicals, carbon-based materials and advanced thermally stable jet fuels. We are taking an integrated approach for both non-fuel and fuel uses that make effective uses of the unique structural features of coals. The non-fuel uses of coal has been discussed at length in our previous reviews that were written in response to the invitations by the late Prof. Frank Derbyshire [Song and Schobert, 1993, 1996].

2. SPECIALTY CHEMICALS

Coal-derived liquids contain various 1-ring to 4-ring aromatic structures. Many of the 2-4 ring structures are not readily available from petroleum, and thus the coal tars are still the major sources of the 2- to 4-ring aromatic chemicals in the world today. Our attention on chemicals has focused on shape-selective catalytic synthesis of value-added chemicals from polycyclic aromatic compounds that are rich in coal liquids and some refinery streams. As outlined in recent reviews [Song, 1998, 1999], we are studying ring-shift isomerization of phenanthrene derivatives to anthracene derivatives, shape-selective alkylation of naphthalene, shape-selective alkylation of biphenyl, conformational isomerization of cis-decahydronaphthalene, and shape-selective hydrogenation of naphthalene, and regio-selective hydrogenation of hetero-aromatic compounds, as described below.

Ring-Shift Isomerization. Phenanthrene and its derivatives are rich in various coal-derived liquids such as coal tars, but their industrial use is still very limited. On the other hand, anthracene and its derivatives have found wide industrial applications. We have found that some mordenite and ion-exchanged Y zeolite catalysts selectively promote the transformation of sym-octahydrophenanthrene (sym-OHP) to sym-octahydroanthracene (sym-OHAn), which we call ring-shift isomerization, as shown in Scheme I. The selectivity and activity of the catalysts also depend on the reaction conditions. This reaction is in distinct contrast to the well-known ring-contraction isomerization which results in methylindane-type products.

Scheme I



sym-OHP **sym-OHAn**

Under mild conditions, some zeolites can afford over 90% selectivity to sym-OHAn with 50% conversion of sym-OHP. This could provide a cheap route to anthracene and its derivatives, which are valuable chemicals in demand, from phenanthrene that is rich in liquids from coal. Possible uses of sym-OHAn include the manufacturing of anthracene (for dyestuffs), anthraquinone (pulping agent), and pyromellitic dianhydride (the monomer for polyimides such as Du Pont's Kapton).

Shape-selective alkylation of naphthalene. Due to the demand for monomers for making the advanced polymer materials such as PEN and PBN, 2,6-dialkyl substituted naphthalene (2,6-DAN) is needed now for making the monomers for PEN, PBN and LCPs. In tars or liquids derived from coal, naphthalene and its derivatives are major components. Shape-selective alkylation over molecular sieve catalysts can produce 2,6-DAN. There are ten possible DAN isomers (Scheme II). The β,β-selective alkylation over molecular sieve catalysts can produce 2-alkylnaphthalene, 2,6-, 2,7-, and 2,3-DAN [Frankel et al., 1986; Komatsu et al., 1994]

The key challenge is to obtain 2,6-DAN with high selectivity, which means increasing the ratio of 2,6/2,7-DAN. Many reports have been published on synthesis of 2,6-DIPN (diisopropylnaphthalene) [Katayama et al., 1991; Moreau et al., 1992] because isopropylation can give much higher selectivity to the 2,6-isomer than the methylation, and an excellent review has been published by Sugi and Kubota [1997]. The results from our laboratory showed that by using partially dealuminated mordenite catalysts, selective alkylation of naphthalene can be achieved with over 65% selectivity to 2,6-DIPN by using isopropanol with 2,6-DIPN/2,7-DIPN ratio of about 3 or using propylene as the alkylating agent with 2,6-DIPN/2,7-DIPN ratio of >2. We also found some simple and effective methods for enhancing the shape selectivity to 2,6-DIPN by using water and chemically dealuminated mordenite.

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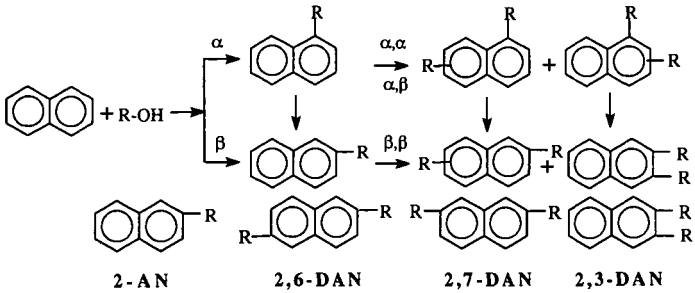
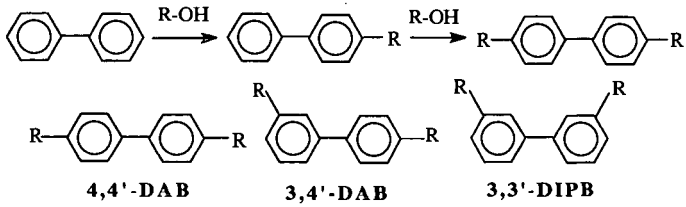
Scheme II



Shape-selective Alkylation of Biphenyl. Biphenyl and its derivatives are present in coal-derived liquids, although at concentrations lower than those of naphthalene derivatives. Shape-selective alkylation of biphenyl (Scheme III) can produce 4,4'-dialkyl substituted biphenyl (4,4'-DAB), the starting material for monomer of some LCP materials represented by Xydar. Proton-form mordenite can be used as shape-selective catalyst for isopropylation of biphenyl.

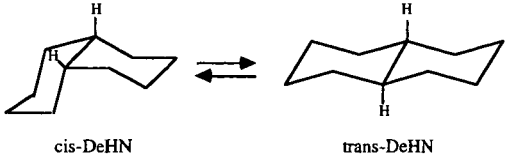
Lee et al. [1989] first demonstrated the beneficial effect of dealumination for selective formation of 4,4'- diisopropylbiphenyl (4,4'-DIPB). Sugi and coworkers have carried out a series of studies on biphenyl isopropylation over mordenites [Sugi and Kubota., 1997]. They have reported on the influence of propylene pressure, effects of SiO_2/Al_2O_3 ratio of mordenites, on shape-selectivity and coke deposition, and impact of cerium exchange of sodium mordenite. It was shown in our report that dealumination of some commercial mordenites by acid treatment first increases then decreases their activity, but increases their selectivity toward 4,4'-DIPB in isopropylation with propylene. More recently, we have found that addition of water to dealuminated mordenite is a simple method to inhibit deactivation of the partially dealuminated mordenite catalysts without losing activity and selectivity.

Scheme III



Conformational Isomerization. Commercial decalins obtained from naphthalene hydrogenation are almost equimolar mixtures of cis-decalin and trans-decalin. In the course of studying sym-OHP isomerization using decalin as solvent, we accidentally found that cis-decalin isomerizes to trans-decalin over ion-exchanged Y zeolite and mordenite catalysts at low temperatures (250°C), as shown in Scheme IV. This reaction would require a temperature of above 400°C in the absence of a catalyst.

Scheme IV



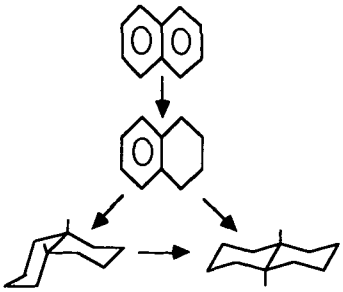
The catalytic reactions were mainly conducted at 200-250 °C for 0.15-8 h under an initial pressure of 0.79 MPa N_2 or H_2 using six catalysts: a hydrogen Y zeolite, a lanthanum ion-exchanged Y zeolite, a hydrogen mordenite, and three noble metal loaded mordenites. Pt- and Pd-loaded mordenites displayed the highest selectivity towards trans-DeHN (nearly 100%), with a trans-DeHN/cis-DeHN ratio of about 13 under H_2 at 200°C; however, they are less effective under N_2. Pre-reduction of Pt/HM30A could improve its catalytic effectiveness in N_2 atmosphere.

By using mordenite-supported platinum or palladium catalysts, it is possible to achieve over 90% conversion with 95% selectivity at 200°C. trans-Decalin has substantially higher thermal stability at temperatures above 400°C. Possible applications of this process are high-temperature heat-transfer fluids and advanced thermally stable jet fuels, which can be used both as heat sinks and as fuels for high-Mach aircraft.

Shape-Selective Hydrogenation of Naphthalene. Complete hydrogenation of naphthalene in conventional processes produces mixtures of cis- and trans-decalin. Our work on selective naphthalene hydrogenation is motivated from the accidental finding on zeolite-catalyzed isomerization of cis-decalin and from the need to tailor the formation of desired isomers from two-ring compounds. Our previous studies on naphthalene hydrogenation showed that certain catalysts

show higher selectivity towards cis-decalin or trans-decalin. More recently, we found that mordenite and Y zeolite-supported Pt and Pd catalysts can selectively promote the formation of cis-decalin or trans-decalin, as shown in Scheme V.

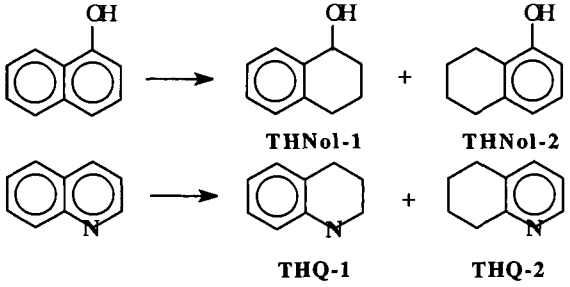
Scheme V



Now we can produce cis-decalin, with over 80% selectivity (or over 80% trans-decalin) at 100% conversion by using some zeolite-supported catalysts at 200°C. cis-Decalin may have potential industrial application as the starting material for making sebacic acid. Sebacic acid can be used for manufacturing Nylon 6,10 and softeners. There is also an industrial need for selective production of tetralin, a hydrogen-donor solvent, from naphthalene. Partial passivation of some zeolite-supported noble metal catalysts by sulfur can make them highly selective for the production of tetralin during metal-catalyzed hydrogenation of naphthalene at low temperatures.

Regio-Selective Hydrogenation. More recently we have begun to explore regio-selective hydrogenation of heteroatom-containing aromatic compounds. Examples of such compounds are 1-naphthol and quinoline shown in Scheme VI. Partial hydrogenation of 1-naphthol can give 1,2,3,4-tetrahydro-1-naphthol (THNol-1) and 5,6,7,8-tetrahydro-1-naphthol (THNol-2). Under fuel hydrotreating conditions, hydrogenolysis of C-O bond can also take place. It is of interest to see whether we can selectively produce THNol-1. We are conducting experimental work on regio-selective hydrogenation over various metal catalysts supported on zeolites, alumina and titania. As in the case of naphthalene hydrogenation described above, the type of metal and support were found to be important for achieving regio-selectivity (for example, to THNol-1) (Shao et al., 2000). Similarly, for partial hydrogenation of quinoline, either 1,2,3,4-tetrahydroquionoline (THQ-1) or 5,6,7,8-tetrahydroquionoline (THQ-2) can be produced. It is interesting to clarify how can one of the two isomers be produced selectively under practically useful conditions for catalytic processing. The hydroaromatic products of regio-selective hydrogenation have some unique applications, e.g. as hydrogen donors or radical scavengers for stabilizing fuels at high temperatures [Andresen et al., 1999; Venkatraman et al., 1998].

Scheme VI



3. CARBON MATERIALS

Since all coals are carbon-rich solids, they are potential starting materials for other, higher value materials via conversion to new carbon-based solids. It is now well known that various useful carbon-based materials and composite materials can be made from coals, coal tars, petroleum pitch, and coal liquids from liquefaction and coal pyrolysis, as shown in Table 1 [Song and Schobert, 1993].

Table 1. List of Some Coal-Based Carbon Materials

Materials That Can be Made Using Coal	Materials from Coal-derived Liquids
Metallurgical coke	Pitch-based carbon fibers
Activated carbon adsorbents	Mesocarbon microbeads
Molecular sieving carbons	Carbon Electrodes
Graphite and graphite-based materials	Binder pitches
Composite (coal/polymer) materials	Activated carbon fibers
Fullerenes or "bucky-balls"	Mesophase-based carbon fibers
Carbon nano tubes	Carbon whiskers or filament
Diamond-like films	Carbon fiber reinforced plastic
Intercalation Materials	Carbon-based Honeycomb

Production of activated carbons from coals has been of interest for years. Excellent reviews, with abundant historical information, has been published by Derbyshire and colleagues [Derbyshire et al., 1995; Derbyshire, 1998]. Activated carbons are used mainly as adsorbents for liquid- and gas-phase applications. The amount of coals used worldwide for producing activated carbons is about 200,000 t/y [Golden, 1992], a significant fraction of the world's annual production of activated carbons, estimated to be about 450,000 t from all feedstocks. Significant growth potential exists for this application, primarily for water and air purification. The liquid-phase applications of activated carbons produced from bituminous coals by chemical activation include water purification, decolorizing, food processing, and gold recovery; the gas-phase applications cover air purification, gas treatment, and solvent recovery [Jagtoyen et al., 1993]. Activated anthracites produced by air treatment prior to steam activation are microporous with a significant fraction of the pores having molecular dimensions [Gergova et al., 1995]. This suggests that molecular sieve materials could be produced from anthracites.

Current graphite technology uses petroleum cokes as the filler material. Molded graphite articles have a wide range of applications, from high-tonnage uses as electrodes in electric arc furnaces, a $US2.2 billion business in 1991 [Pierson, 1993], to specialty graphites for high-technology uses in chemical vapor deposition and epitaxial deposition devices. Meta-anthracite, of very limited value (≈$US25/ton) because of its poor combustion performance, may be a superior filler for molded graphites, even better than the more conventional anthracites. For example, non-catalytic graphitization of meta-anthracite at 2400°C yields a product having a 0.3363 nm d-spacing [Morrison et al., 1996], compared with the 0.335 nm value of pure graphite. The value of meta-anthracite as a replacement for petroleum coke in graphite production would exceed its value as a fuel by about a factor of ten.

The amount of coals used worldwide for producing molecular sieving carbons (MSC) is estimated to be 3,000 tonnes/year [Golden, 1992]. The application MSC for gas separation by pressure-swing adsorption is now commercially viable. In the United States, MSC is used for air separation by Air Products and Chemicals Inc. It is likely that more companies will be engaged in producing MSC in the next century.

Coal tar pitches are raw materials for carbon fibers and mesocarbon microbeads [Derbyshire et al., 1994]. Liquids from coal extraction and liquefaction can be used for making carbon fibers and graphitic materials [e.g., Zondlo et al., 1993]. Kimber and Gray [1976] also noted potential advantages in using coal-based coke for making carbon electrodes.

4. ADVANCED JET FUELS

One commercially available route to make liquid fuels from coal is the well-known SASOL route incorporating coal gasification as the first step and the Fischer-Tropsch synthesis as the second step. The fuels from Fischer-Tropsch synthesis using either natural gas- or coal-derived syngas are good as diesel fuels. However, for jet fuel applications, there is an unique structural advantage of coal that can lead to superior fuels. There are some unique compositional advantages of coal-derived liquids for making jet fuels, with respect to the high-temperature thermal stability required for future supersonic and hypersonic jet aircraft. The USAF has established a long-term goal to develop advanced jet fuels called JP-900 that are stable at high temperatures up to 900 °F (482 °C) [Edwards et al., 1997].

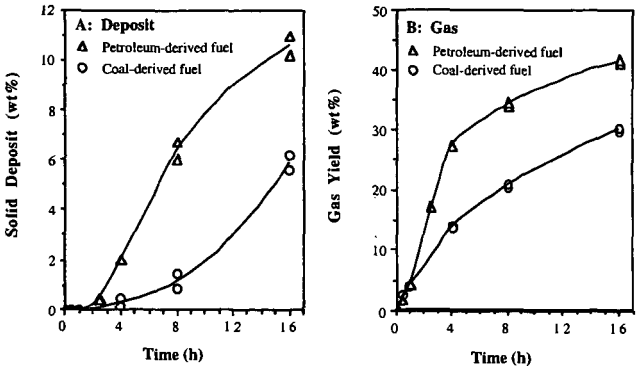


Figure 1. Formation of solid deposit (A) and gases (B) from petroleum-derived JP-8P and coal-derived JP-8C jet fuels at 450°C for 0.5-16 h under nitrogen atmosphere (100 psi, cold).

As can be seen from Figure 1, compared to conventional petroleum derived jet fuels, the coal-derived jet fuels display greater thermal stability at temperatures above 400 °C in the pyrolytic regime, in terms of much lower degree of decomposition and significantly less amount of solid deposit [Lai et al., 1992; Song et al., 1993]. This is because coal-derived jet fuels are rich in cycloalkane and the aromatic compounds in coal-derived jet fuels can be dominated by hydroaromatic structures. Cycloalkanes are more stable than the n-alkanes with the same or less carbon number, and the stability of alkylated cycloalkanes decreases with increasing length or carbon number of the side chain [Lai and Song, 1996; Song and Lai, 1998]. At temperatures above 400°C, decomposition of long-chain paraffins in jet fuels is dominated by radical-chain reactions [Song et al., 1994a]. Hydroaromatic compounds such as tetralin are hydrogen donors which can serve as radical

scavengers in pyrolytic reactions which inhibit the thermal decomposition of reactive hydrocarbons [Song et al., 1994b; Yoon et al., 1996]. Studies on model paraffinic jet fuels in the absence and the presence of added hydroaromatic compounds have also demonstrated that they are capable of suppressing the initial decomposition by retarding the radical reactions [Venkatraman et al., 1998; Andresen et al., 1999].

Coal-derived JP-8C fuel and a model jet fuel that contains mainly cycloalkanes and about 10% tetralin has been shown to be thermally stable at temperatures up to 482°C or 900 °F [Strohm et al., 1999].

The coal-based thermally stable jet fuels can be produced using liquids that are partially or wholly derived from coal, by one of the following strategies: (1) the use of by-product coal tars from coal carbonization or from coal gasification (pyrolysis); (2) the use of blends of coal tar distillates and petroleum refinery streams, which would enlarge the pool of available feedstock; (3) the use of by-product liquids from co-coking of coal and petroleum resids; and (4) the use of liquids from co-processing of coal and petroleum resids, which is a process alternative to the well-known direct liquefaction of coal.

5. CONCLUDING REMARKS

We must always keep in mind that coal is a valuable hydrocarbon source, that can have multiple and equally important uses for both non-fuel and fuel applications. As we move into the 21st century, coal may become more important both as an energy source and as the source of chemical feedstocks.

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CATALYTIC HYDROTREATMENT OF HETEROATOM SPECIES IN SOUTH BANKO COAL LIQUID DISTILLATE OVER CARBON SUPPORTED NiMo CATALYST

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Abstract

Hydrotreatment of crude liquid oil produced from South Banko coal (SBCL) was carried out using alumina and carbon supported NiMo catalysts to find advantages of carbon support for up-grading coal liquid. Reactivity of representation sulfur, nitrogen and oxygen molecular species were measured to confirm the high activity of the catalyst against refractory species. NiMo supported on of ultrafine particle carbon black (Ketjen Black:KB) with extremely large surface area was found an excellent support for hydrotreatment catalyst to show much higher activity for the hydrodesulfurization(HDS), hydrodenitrogenation(HDN) and hydrodeoxygenation(HDO) of coal liquid than that of a commercial NiMo/Al2O3 catalyst.

Key words: coal liquids oil, hydrotreatment, carbon support catalyst

Introduction

As environmental protections become greater concern, it is very essential to treat hydrocarbons feed-stocks such as naphthas, middle distillate, gas oil, vacuum gas oil, vacuum resids, coal liquids to decrease the content of undesirable aromatic hetero atomic species. Noble metal catalysts, which are excellent for aromatics saturation, get fast poisoned by the sulfur and nitrogen compounds to lose their activity.

The support to replace alumina is one of targets approaches for this purpose. Carbon has been recognized an interesting support to showing higher catalytic activity for the HDS of thiophene than alumina support [1]. Such high activity of carbon-supported HDS catalyst has been attributed to the inertness of the carbon support as compared to the conventional alumina support [1]. Carbon has the additional advantage over other support of a great flexibility in the modification of both the porosity and surface area. Daly et al [2] have shown that the types of carbons affected the distribution of active sulfides on their surface. Vissers et al. [3] found that increasing of carbon surface area results in increasing HDS activity because of the lower sintering trend of the active phase. Schmitt and Castellion [4] also found that sulfides supported on carbon with larger mean pore size were more active for the HDS of gasoil. Drahoradova et al. [5] reported that NiMo on carbon showed higher hydrodenitrogenation (HDN) activity and lower inhibition of HDS activity with thiophene/pyridine feeds than alumina-supported NiMo. Mochida et al [6], also notified that nickel molybdenum sulfide supported on carbon (Ketjen Black) was more active for the hydrogenation of 1-methylnaphthalene than NiMo supported on alumina. Furthermore, carbon-based catalysts can be less expensive than alumina. Combustible carbon facilitates metals recovery and reduced volume of disposal [7].

The present study prepared KB supporting nikel-molibdenum sulfide catalyst and applied to the hydrotreatment of SBCL which contained much more aromatic and hetero atom species such nitrogen, sulfur and oxygen sompounds. Its activity for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) was compared with those of a commercially available alumina catalyst to find the advantages of carbon support in the hydrotreatment of highly polar feed.

Experimental

Feed

The sample used were two different cutting point of SBCL (A: bp < 300 °C; B: bp 200 ~ 350 °C) which was prepared at 450 °C, 15 Mpa using limonite catalyst in a BSU (Bench Scale Unit) pilot plant of Nippon Brown Coal Liquefaction Co. Ltd. and was supplied by courtesy of NEDO. Their properties are listed in Table 1.

Catalyst

A commercially available NiMo/ Al2O3 (NiO; 2 wt%, MoO3; 10 wt%), was used as a reference. Carbon supported NiMo catalyst was prepared in the laboratory. Some properties of carbon black (Ketjen Black:KB EC 600JD) provided by Mitsubishi Chemical Co. are summarized in Table 2. Nickel and Molybdenum salt were impregnated simultaneously using Ni(Ac)2 and MoO2-AA in methanol. Ni(Ac)2 and MoO2-AA dissolved in methanol were mixed to the slurry KB methanol and were dispersed by ultrasonic for 40 min. The mixture was heated up to 40 °C for 120 min, followed by evaporation to remove solvent under reduced pressure. The catalyst precursor was then dried at 120 °C for 12 h in vacuum. It was presulfided in a 5 % of H2S/H2 flow at 360 °C for 2 h prior to the reaction.

Hydrotreatment procedures

Hydrotreatment of South Banko coal liquid distillate was performed in a 50ml magnetically stirred autoclave. The ratio of catalyst to feed was 10 wt%, and 10 g of feed was used. Feed was charged in to the autoclave together with catalyst, and the autoclave was flush with nitrogen three times to replace air and was then filled with pure hydrogen. The initial pressure of hydrogen was 10 MPa. The reaction time was counted from the point when the reaction temperature was reached to the prescribed temperature. The hydrogenated product was collected from the autoclave with acetone. The liquid product was then separated from the catalyst by vacuum filtration. After removal of acetone, the hydrogenated product was analyzed by GC-AED to calculate the extent of HDS, HDN and HDO.

Results

GC=AED chromatographs of SBCL (A) before and after hydrotreatment at 360 °C over NiMo/Al2O3 catalyst are illustrated in Figure 1 ~ 3. Figure 1 shows high reactivity of sulfur species, which allowed them complete removal under this condition. Nitrogen exhibited the lower reactivity and still much reminded after the reaction as shown in Figure 2. Pyridines were the most reactive among nitrogen species. The nitrogen species left in the hydrotreated oil were found as anilines, methyl-, dimethyl, trimethyl-anilines, quinoline and indoles. The oxygen compounds were further less reactive than other heteroatoms species as shown in Figure 3. Most of phenols still remained after the hydrotreatment over NiMo/Al2O3 catalyst at 360 °C. Dibenzofuran appeared the most refractory species.

Figure 4 & 5 illustrate both reactivities of SBCL (B) in the hydrotreatment at 360 °C over NiMo/Al2O3 and NiMo/KB. SBCL (B)of higher boiling range carried much less reactive species such as 4,6-dimethyldibenzothiophene and dimethylcarbazoles. Hence their heteroatom removal was much slow than that of SBCL (A). The carbon-supported catalyst was found more active than alumina supported one, shows better removal all heteroatoms. The advantage of carbon support decreases in order of S > N > O removal.

Discussion

The reactivity of heteroatom species in SBCL (A) is defined clearly in the order of S > N > O. Sulfur was easily removed became smaller content and least refractory species such as 4,6-dimethyldibenzothiophene. Nitrogen species are less reactive than sulfur species. Among the nitrogen species, very basic nitrogen species were removed at lower temperature, their

preferential adsorption being suggested. Anilines and alkyl anilines were less reactive. Oxygen species especially benzofuran were very unreactive.

KB supported NiMo catalyst was found much more active than alumina supporting ones especially against refractory species. Large surface area and very fine grains help its high dispersion of active phases over the surface and among the heteroatom species of the catalyst particles. The number of active site is believe to depend on the extent of sulfurization. Medium strength of chemical interaction between active phase and carbon support may be favorable for complete sulfurization.

The acidic polar support has been believed to help hydrogenation and C-X cleavage. It clear accelerates the deactivation by coking through strong absorption. Carbon is certainly expected less deactivated. More chemical modification of carbon can be the target of the next research.

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Table 1 Elemental analyses of feed

Sample	b.p(°C)	C*	H*	N*	S**	O***	H/C
A	< 300	84.97	10.37	0.84	667	3.74	1.46
B	200 - 350	85.59	9.09	1.74	770	3.49	1.27

* : wt%, ** : ppm, *** : differences

Table 2 Some Properties of Ketjen Black

Surface area (m^2/g)	1270
Volatile matter (%)	0.7
PH	9.0
Particle size (nm)	30
Apparent density (g/L)	115
Ash (%)	0.1
Ni (ppm)	1.5
V (ppm)	30
Fe (ppm)	100
Cu (ppm)	1
Mn (ppm)	1

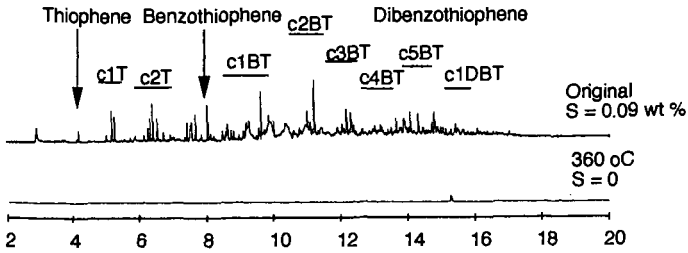

Figure 1 sulfur chromatograms of hydrotreated SBCL (A) over NiMo/Al2O3 catalyst

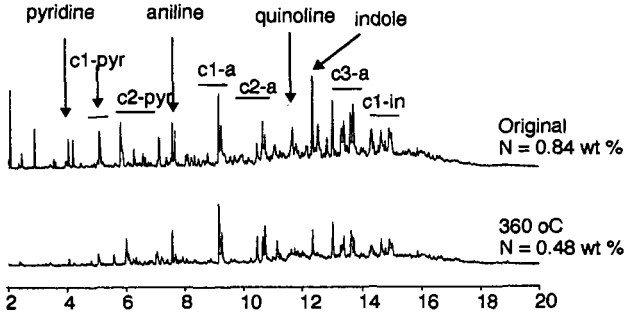

Figure 2 nitrogen chromatograms of hydrotreated SBCL (A) over NiMo/Al2O3 catalyst

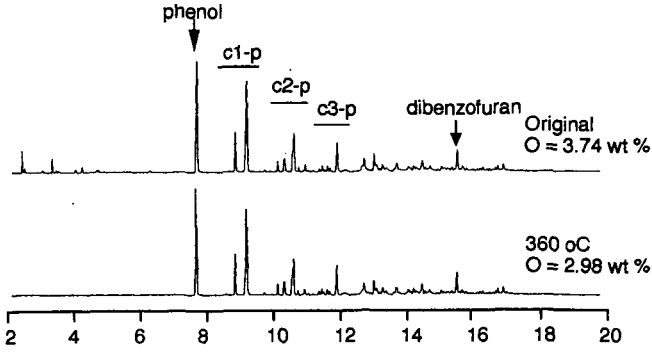

Figure 3 oxygen chromatograms of hydrotreated SBCL (A) over NiMo/Al2O3 catalyst

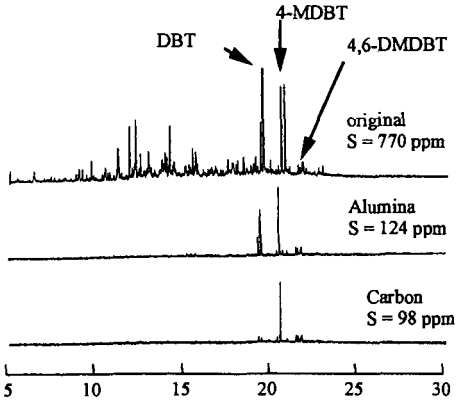

Figure 4 sulfur chromatogram of hydrotreated SBCL(B) over NiMo/Al2O3 and NiMo/carbon catalyst

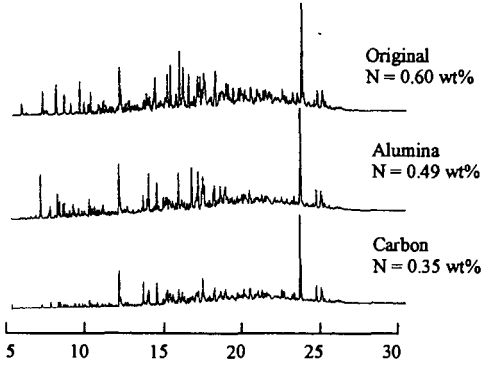

Figure 5 Nitrogen chromatograms of hydrotreated SBCL(B) over NiMo/Al2O3 and NiMo/carbon catalyst

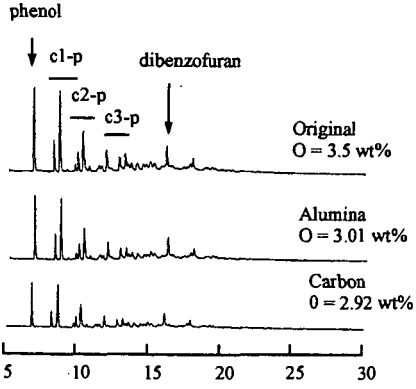

Figure 6 oxygen chromatographs of hydrotreated SBCL(B) over NiMo/carbon and NiMo/Al2O3 catalyst

ENHANCING ACTIVITY OF IRON-BASED CATALYST SUPPORTED ON CARBON NANO PARTICLES BY ADDING NICKEL AND MOLYBDENUM

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Abstract

FeMoNi catalyst supported on carbon nanoparticles (Ketjent Black: KB) was tested in the liquefaction of sub-bituminous coals in an autoclave of 50 ml capacity. At 450^{0}C and 15 MPa, the liquefaction of (an Indonesian coal) Tanito Harum coal with FeMoNi/KB catalyst (10% Fe, 5% Mo, 2% Ni, 83% KB) provided oil yield as high as 77wt% that is comparable to that obtained from liquefaction with NiMo/KB catalyst (2% Ni, 10% Mo, 88% KB). The ternary catalyst was also optimized for the highest activity in terms of loading amount and order of the active components.

Keywords: coal liquefaction; iron molybdenum nickel catalysts; carbon nanoparticle support

Introduction

In fundamental research, a number of catalytic materials have been examined to find better liquefaction catalyst. However, only iron and molybdenum have been attempted in demonstration plant and so far the greatest attention has been given to Fe catalysts because of their low cost and disposability even though their activity is rather poor. To enhance the activity of iron, active metals of higher price have been combined by expecting some synergistic activation. Moreover, the very fine particles as catalyst supports having high surface area are useful to give high dispersion of active metals on its surface. In addition, as carbon support, it has a weak interaction between the metal phase and the support, which allows the quantitative conversion of the metal oxide to the active sulfide form. Thus, the carbon-supported catalysts are very effective to carry more active and costly metals at lower loading.[1]

The present authors have attempted to use the nickel-molybdenum sulfide supported on carbon nano particles (KB: Ketjen Black) to achieve excellent activity and recovery for repeated use in the liquefaction.[2] The authors also proposed FeNi sulfide on KB to reduce the cost of catalyst, which is superior to the NiMo/Al_2O_3 but inferior to the NiMo/KB.[3,4]

In the present study, catalytic activities of ternary sulfide FeNiMo/KB were examined by loading least amount of Mo on carbon nanoparticles to obtain the activity that is comparable to that of NiMo/KB catalyst. The effect of catalyst preparation method to the activity of FeMoNi/KB catalyst was also investigated.

Experimental Section

Catalyst and Materials

Fe, Ni and Mo salts were impregnated on to KB by several impregnating methods using $FeC_4H_2O_4$ (fumarate), $Ni(NO_3)_2$ or Ni-$(Ac)_2$, and MoO_2-AA in methanol and water depending on the solubility of the salts. The catalysts prepared in the present study are listed in Table 1. A prescribed amount of Ketjen black (KB) was dispersed in methanol under ultrasonic irradiation for 15 min. A mixture of iron(II) fumarate and $Ni(NO_3)_2$ dissolved in methanol was mixed to the KB-methanol slurry with a small amount of nitric acid (1% vol.) as an additive. The slurry had been dispersed under ultrasonic irradiation and heated at 40^0 C for 2 h before the slurry was evaporated, and dried at 120 ^{0}C for 12 h in vacuo. In the case of successive impregnation, nickel was first impregnated, being followed by iron. Other combinations of metal precursors, Mo/Ni, Fe/Mo, and Fe/Mo/Ni (the order of impregnation) were also impregnated on KB. These catalysts were presulfided by flowing 5% vol H_2S/H_2 at 360^0 C for 2 h prior to the reaction.[2,3,5]

The elemental analyses of Tanito Harum, Yilan, and Shenmu coals are summarized in Table 2. Commercially guaranteed grade tetralin (TL) was used as a liquefaction solvent, and 1-methylnapthalene was used as a reactant in the hydrogenation.

Liquefaction Procedure.

Coal liquefaction was performed in an electromagnetic-driven autoclave of 50 ml capacity. 3 g of coal, 3 g of solvent and 0.09 g of catalyst were charged to the autoclave[6]. The liquefaction was performed under 15 MPa of hydrogen pressure at 450^{0}C for 60 min. The heating rate to the reaction temperature was 20^{0}C/min, and the stirring speed was 1300 rpm.

The liquid and solid products of coal liquefaction were recovered by THF. After the THF was removed by evaporation, the product was extracted in sequence with n-hexane, acetone, and THF. The n-hexane-soluble (HS), n-hexane-insoluble but acetone-soluble (HI-ACS), acetone-insoluble but THF-soluble (ACI-THFS), and THF-insoluble (THFI) substances were defined as oil (O) and

solvent, asphaltene (A), preasphaltene (PA), and residue (R), respectively. The gas yield was calculated by the weight difference between initial coal, solvent, and recovered product. The oil yield was calculated by subtracting the initial solvent weight from the total weigh of HS. The reaction under the same conditions was repeated at least three times to make sure the experimental results that were within the errors of 1wt% daf coal base.

Hydrogenation of 1-methylnapththalene.

1-Methylnaphthalene (1-MN; 6g) and catalyst (1.5wt% based on 1-MN) were charged into a 50 ml magnetically stirred autoclave. Standard conditions for the hydrogenation were 60 min , 360^{0}C, and 15 MPa of H_2 reaction pressure. The 1- and 5-methyltetralins and trace of tetralin were identified and quantified by GC-MS to calculate the hydrogenation activity and selectivity over the catalyst.

Results and Discussion

Effects of Ni or Mo on the catalytic activities of iron supported on KB.

Figure 1 describes yields of Tanito Harum coal liquefaction at 450^{0}C and 15 MPa with Fe(10%) based catalyst on KB. The addition of Mo from 2 to 3% improved the oil yield of 67 and 68% , respectively, which were much higher than that of Fe(20)/KB. FeNi/KB catalyst with Ni content of 15% provided oil yield as high as 73%. More Mo or Ni content tends to increase the activity of Fe based catalyst.

Activity of the NiMo/KB catalysts with various Mo content and effects of Ni addition to the FeMo/KB catalyst

Figure 2 shows the activity of NiMo/KB catalyst with various Mo contents and the effect of Ni addition to the FeMo/KB catalyst in the liquefaction of Tanito Harum coal. The activity of NiMo/KB catalyst increased in line with the increase of Mo content in the catalyst. The Ni Mo/KB catalyst with Mo content of 10% provided a very high oil yield of 78%.

The activity of FeMo/KB catalyst was improved by the addition of Ni. Fe(10)Mo(3)Ni(3)/KB gave higher oil yield than that of Fe(10)Mo(3)/KB (see Fig. 2e and 1c). The activity was governed by Mo content of 2 to 5% that provided oil yield from 70 to 77%. It must be noted that 5% Mo in FeMoNi/KB catalyst provided a comparable oil yield to that of Ni(2)Mo(10)/KB under the same conditions. Moreover, 3 and 5% Mo in FeMoNi/KB gave oil yield of 5% higher than those of NiMo/KB with the same as Mo contents.

Effects of catalyst preparation procedure on the catalytic activity of NiMo and FeMoNi on KB

Figure 3 shows the effects of catalyst preparation procedures. For NiMo/KB catalyst, successive impregnation method appeared definitely much better than simultaneous impregnation. In impregnation procedure, molybdenum was first impregnated. However, the order of Mo/Fe/Ni in the successive method gave the same oil yield as to that in simultaneous impregnation procedure (see Figure 3c and 3d), while the order of Fe/Mo/Ni provided a slightly higher oil yield (see Figure 3e). Successive impregnation appears to give higher activity when the most dominant metal component was loaded. The reason is that the metal component is generally better dispersed in the first impregnation than in the second one because the component gets more space on the support. However, the effects in the successive impregnation may not be so strong for the component of inferior majority such as Fe.

Comparison of various catalysts in the liquefaction of Yilan and Shenmu coals

Figure 4 compares the activities of FeNi/KB, FeMoNi/KB, NiMo/KB catalysts in the liquefaction of Yilan and Shenmu coals. The activities of Fe(10)Ni(10)/KB, Fe(10)Mo(3)Ni(3)/KB, Ni(2)Mo(10)/KB catalysts in the liquefaction of Yilan coal provided 65%, 72%, and 77% oil yields, respectively. FeMoNi/KB catalyst with less Mo content gave much higher oil yields than FeNi/KB catalyst. High oil yield compensated by low gas, asphaltene, and preasphaltene yields suggests high selectivity of FeMoNi/KB catalyst. In the liquefaction of Shenmu coal (bituminous coal), the oil yield by FeMoNi/KB catalyst was higher compared to FeNi/KB in spite of lower than that of NiMo/KB catalyst.

The activity of NiMo and Fe based catalysts supported on KB in the hydrogenation of 1-methylnaphthalene

Table 3 compares the activities of catalysts in the hydrogenation of 1-methylnaphthalene at 360 ^{0}C, 15 MPa H_2, and 60 min. The Mo content governed basically the hydrogenation activity. The Mo content of 2, 3, 5, and 10% in the Fe-based and NiMo catalysts on KB provided conversions of 16, 24, 47, and 94%, respectively, regardless of the other components. The catalysts prepared by successive impregnation procedure showed a little better activity than that by simultaneous impregnation.

Conclusion

The addition of small amount of molybdenum and nickel on the iron catalyst supported on carbon nanoparticles enhances the activity of the catalyst in the liquefaction of sub-bituminous and bituminous coals. However, the hydrogenation activity for aromatic ring of the catalyst is basically influenced by Mo content. The activity of FeMoNi/KB catalyst is slightly influenced by the order of impregnation sequences in the catalyst preparation procedure.

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Table 1. Catalysts and Salts

Catalysts[a]	Fe salts	Ni salts	Mo salts
1. Fe(10)Ni(10)	$FeC_4H_2O_4$	$Ni(NO_3)_2$	-
2. Fe(10)Ni(15)	$FeC_4H_2O_4$	$Ni(NO_3)_2$	-
3. Fe(10)Mo(2)	$FeC_4H_2O_4$	-	MoO_2-AA
4. Fe(10)Mo(3)	$FeC_4H_2O_4$	-	MoO_2-AA
5. Fe(10)Mo(2)Ni(2)	$FeC_4H_2O_4$	$Ni(NO_3)_2$	MoO_2-AA
6. Fe(10)Mo(3)Ni(3)	$FeC_4H_2O_4$	$Ni(NO_3)_2$	MoO_2-AA
7. Fe(10)Mo(5)Ni(2)	$FeC_4H_2O_4$	$Ni(NO_3)_2$	MoO_2-AA
8. Ni(3)Mo(3)		$Ni\text{-}(Ac)_2$	MoO_2-AA
9. Ni(2)Mo(5)		$Ni\text{-}(Ac)_2$	MoO_2-AA
10. Ni(2)Mo(10)	-	$Ni\text{-}(Ac)_2$	MoO_2-AA

[a] Numbers in parentheses indicate the weigh percent of metals.

Table 2 Elemental Analysis of Coals Used in The Present Study

	C[a]	H[a]	N[a]	O[a]	S[a]	Ash[b]	H/C	O/C
Tanito Harum Coal	71.2	5.5	1.6	21.7	0.16	3.9	0.93	0.23
Yilan Coal	76.1	5.6	1.3	16.7	0.22	3.8	0.88	0.167
Shenmu Coal	78.8	5.1	1.1	14.7	0.21	3.9	0.78	0.14

[a] in Wt % (d.a.f.)
[b] Wt.% in

Table 3 Hydrogenation of 1- Methylnapthalene [a]

Catalysts	Conversion % [b]
Fe(10)Ni(10)/KB (simultaneous impregnation)	14
Fe(10)Ni(10)/KB (successive impregnation)	16
Fe(10)Mo(2)Ni(2)/KB (simultaneous impregnation)	16
Fe(10)Mo(3)Ni(3)/KB (simultaneous impregnation)	24
Fe(10)Mo(3)Ni(3)/KB (successive impregnation)	28
Fe(10)Mo(5)Ni(2)/KB (successive impregnation)	47
Ni(2)Mo(10)/KB (simultaneous impregnation)	94
Ni(2)Mo(10)/KB (successive impregnation)	98

[a] Catalysts, 0.09 gr; 1-methylnapthalene, 6 g
[b] Reaction conditions : 360 ^{0}C; 15 MPa; 60 min; stirring speed : 1300 rpm.

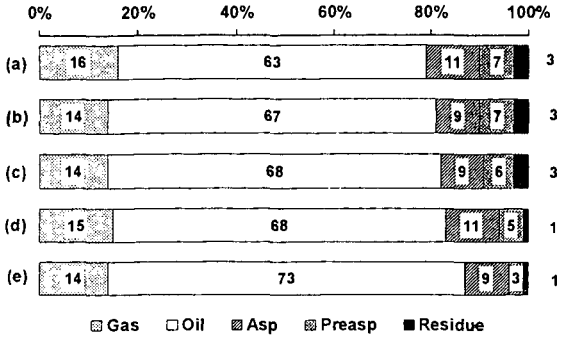

Figure 1. Effect of Ni or Mo addition to the Fe(10)/KB on the liquefaction of Tanito Harum coal : (a) Fe(20)/KB; (b) Fe(10)Mo(2)/KB; (c) Fe(10)Mo(3)/KB; (d) Fe(10)Ni(10)/KB, (e) Fe(10)Ni(15)/KB.

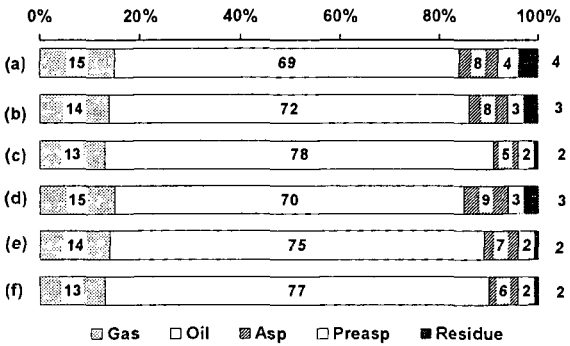

Figure 2. Activity of the NiMo/KB catalysts with variable Mo content and Effect of addition of Ni to the FeMo/KB catalysts on the liquefaction of Tanito Harum coal : (a)Ni(3)Mo(3)/KB; (b) Ni(2)Mo(5)/KB; (c) Ni(2)Mo(10)/KB; (d) Fe(10)Mo(2)Ni(2)/KB; (e) Fe(10)Mo(3)Ni(3)/KB; (f) Fe(10)Mo(5)Ni(2)/KB.

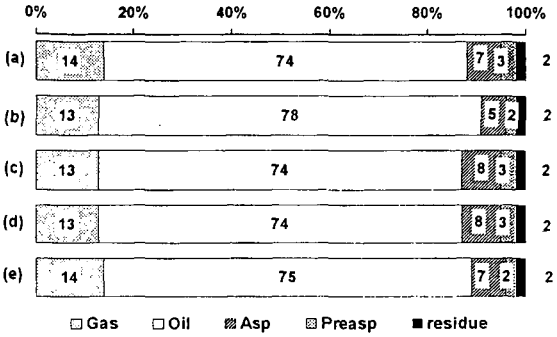

Figure 3 Effect of preparation method on the catalytic activity of Mo-based catalysts in the liquefaction of Tanito harum coal : (a) Ni(2)Mo(10) simultaneous impregnation process; (b) Ni(2)Mo(10) successive impregnation process; (c) Fe(10)Mo(3)Ni(3) simultaneous impregnation; (d) Fe(10)Mo(3)Ni(3) successive impregnation process I* , (e) Fe(10)Mo(3)Ni(3) successive impregnation process II**.

* Mo was firstly impregnated

** Fe was firstly impregnated

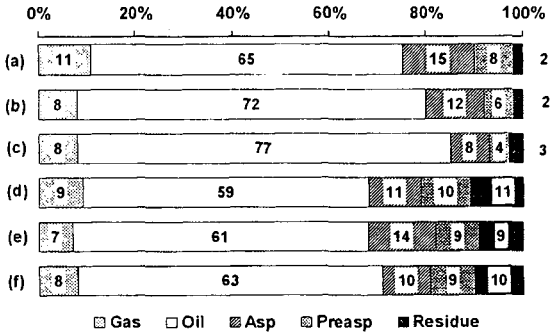

Figure 4 Activities of Fe(10)Ni(10)/KB, Fe(10)Mo(3)Ni(3)/KB, and Ni(2)M0(10)/KB catalyst in the liquefaction of Yilan, and Shenmu coals with tetralin solvent. (a), (b), (c) Yilan coal; (d), (e), (f) Shenmu coal; (a), (d), Fe(10)Ni(10)/KB catalyst, (b), (e) Fe(10)Mo(3)Ni(3)/KB catalyst; (c), (f) Ni(2)M0(10)/KB catalyst.

CO and CO_2 Hydrogenation Over Co/SiO_2 Catalyst

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Summary

CO and CO_2 hydrogenation was studied in a fixed bed reactor on a Co/SiO_2 catalyst. Reaction was carried out at 220°C, 350psig, H_2:CO=2:1, H_2:CO_2 = 2.1, with a total flow rate of 150 mL/min (3NL/hr/g catalyst) and a H_2+CO, H_2+CO_2 or H_2+CO+CO_2 flow rate of 50 mL/min(1NL/hr/g catalyst). CO, CO_2 and CO,CO_2 mixture feed gas were used respectively for comparison. The results indicated that in the presence of CO, CO_2 hydrogenation hardly occurred. For the cases of only CO or only CO_2 hydrogenation, the activity of the two were similar but the selectivity was very different. For CO hydrogenation, normal Fischer-Tropsch synthesis product distribution were observed with an α of about 0.80; in contrast, the CO_2 hydrogenation product contained about 70% methane. Thus, CO_2 and CO hydrogenation appears to follow different reaction pathways.

Introduction

Fixation of carbon dioxide has become of greater interest in recent years, primarily because of its impact on the environment through the greenhouse effect. One approach that has attracted attention is to produce synthesis gas through its reaction with methane even though the syngas produced only has a H_2/CO ratio of 1 for the idealized reaction. Another option is to recycle carbon dioxide to a gasification unit; however, there is a limit to the amount of carbon dioxide that can be utilized in this manner. Another approach is to hydrogenate carbon dioxide in Fischer-Tropsch synthesis (FTS) plants; this has become an attractive approach even though one must find a source of hydrogen to accomplish this.

For high temperature (330-350°C) FTS the water-gas-shift (WGS) reaction is sufficiently rapid that it is nearly at the equilibrium composition. The hydrogenation of CO_2 at high temperatures is possible and occurs in the fluid bed reactors operated by Sasol and Mossgas. However, the use of a slurry phase bubble column reactor is very attractive since its use allows the FTS reaction to be carried out isothermally. In the liquid phase synthesis, lower temperatures must be utilized (220-240°C) with either a cobalt or iron catalyst. It was of interest to compare the FTS reactions of CO and CO_2 with a cobalt catalyst. In this initial work a simple catalyst formulation has been utilized: cobalt supported on a silica without any promoters.

Experimental

The catalyst was prepared by three incipient wetness impregnations of silica (Davisil 644, 100-200 mesh, 300 m^2/g, and pore volume of 1.15 cm^3/g) with aqueous cobalt nitrate to produce a final loading of 15 wt.%. The material was dried in a fluidized bed and then calcined for 4 hrs. in an air flow at 400°C. Three grams of the calcined catalyst was diluted with 15 g of glass beads and placed in a fixed bed reactor where it was reduced in a H_2(33%)/Ar flow for 10 hours at 350°C. The reaction conditions were: 220°C, 24 atm (2.4MPa), H_2/CO = 2/1, 3 NL/hr/g catalyst total gas flow, 1 NL/hr/g catalyst synthesis gas flow. Analysis of the gaseous products was accomplished using gas chromatography.

Results.

The conversion of CO and CO_2 during 10 days on-stream are given in figure 1. Compared to the CO conversions of the same and another similar Co-silica catalyst, it appears that the initial CO conversion is about the same in the CSTR and in the fixed bed reactor; however, the activity decline is more rapid in the fixed bed reactor. The run data and conversions for the fixed bed reactor are compiled in table 1.

There was a decline in activity during the period between collecting the first two samples. The exit gas from the CO_2 conversions contained more CO_2 than the calibration gas so that CO_2

conversions were calculated from the mass balance for the other gaseous and liquid products; thus, there is some uncertainty in the absolute CO_2 conversion data but the trend shown in Table

Table 1 Run conditions and results from the conversion of CO and CO_2 with a cobalt-silica catalyst.

sample No.	time on stream(hrs)	feed gas	conversion(%)
1	17.3	CO	52.2
2	39.47	CO	45.8
3	44.47	CO2	31.2.
4	61.97	CO	24.4
5	70.47	CO2	23.1
6	90.97	CO2	20.5
7	109.97	CO	18.6
8	117.22	CO2	24.5
9	134.47	CO+CO2	CO, 53.5% CO2, 3.98%
10		methanol	
11	206.22	CO+CO2(different flow rate)	CO: 9.86% CO2: 6.1%
12	226.89	CO2	22.8

1 and figure 1 are certainly valid. Thus, with the cobalt catalyst the conversion of CO and CO_2 occur at about the same rate. This is in contrast to the observations with an iron catalyst under low temperature FTS conditions where the rate of conversion of CO_2 is considerably lower than for CO (1-6).

A striking difference for the cobalt catalyst is the formation of methane. Under the same reaction conditions, the amount of methane produced is much higher for the CO_2 reactant (figure 2). Whenever CO_2 was the reactant, methane accounted for greater than 70% (based on carbon). However, under the same reaction conditions and with the same catalyst, methane accounted for less than 10% of the products. Similar results are reported by Riedel et al. (6). This requires that methane be formed by two pathways or that a common reaction intermediate and reaction pathway does not occur with CO and CO_2.

During period 9, the feed was changes so that equal amounts of CO and CO_2 were present in the feed and the flows of Ar, H_2 and (CO + CO_2) were the same as when either pure CO or CO_2 was converted. Under competitive conversions, CO was converted much more rapidly than CO_2, clearly showing that CO is adsorbed on the Co catalyst to a much greater extent than the CO_2. Whereas the total carbon oxide conversion is about the same expected from the trend of the previous runs, the conversion of CO accounted for more than 90% of the total conversion of the carbon oxides. A similar result was obtained following the conversion of methanol except that there was not as dramatic a difference as would be expected from the trend of the previous conversions. The CO conversion following the period of methanol feed was lower than expected from the trend of the prior periods. Since the water partial pressure was much higher during the conversion of methanol, it is anticipated that irreversible, or slowly reversible, damage of the catalyst occurred during the exposure to the high water partial pressure conditions.

Following the first conversion of the mixture of CO and CO_2, methanol was substituted for the carbon oxides feed. Because of the limitations of the liquid pump, the feed during this period was only H_2 and methanol. The total flow was 4 NL/hr/g catalyst and the H_2/methanol molar ratio

was 2/1. Thus, the H2/carbon ratio in the feed was the same as when CO and/or CO_2 was the feed but the flow rate of methanol was four times that of the carbon oxide. Under the reaction conditions used the conversion of methanol was about 50% whereas the conversion of CO or CO_2 was slightly less than 25%. Thus, considering the higher flow rate (4 times higher) and higher conversion (2 times higher) of methanol, the total carbon converted with the methanol feed was about 8 times greater than for the carbon oxides. Thus, the relative rate is rapid enough that any methanol intermediate could be converted to methane so that methanol would not be detected in the liquid sample; unfortunately, in this preliminary run the analysis of the gas sample did not provide a measure of the amount of methanol in the gas phase. The only significant products from the conversion of methanol under the FTS conditions were methane and water; thus, any methanol formed during the reaction could have been converted to methane.

Discussion.

The difference in the product distributions obtained from the hydrogenation of CO and CO_2 preclude a common reaction pathway for FTS unless there is a second reaction pathway for the conversion of CO_2, but not CO, to methane. Furthermore, if there is a second pathway, then the FTS with CO_2 occurs at about only 20% of the rate with CO.

Based on the preliminary data, it is proposed that the conversion of CO and CO_2 occurs by different reaction pathways. It is assumed that the hydrogenation and breaking of the two C-O bonds of the CO_2 provide the source of the different pathways. In this proposal, the breaking of the C-O bond, presumably by the addition of adsorbed H to form C-O-H, competes with, and probably leads, the addition of adsorbed H to form the C-H bond. Thus, for CO the following reaction pathway could apply:

$$C\text{-}O_a + 2\,H_a \rightarrow [\,H\text{-}C\text{---}O\text{-}H\,]_a \rightarrow H\text{-}C_a + O\text{-}H_a \qquad [1]$$

In the case of CO_2 the reaction is more complex since there are two C-O bonds that must be broken prior to, or simultaneous with, the formation of the C-H bond. If it is assumed that similar rates apply for the formation of the first O-H and C-H bonds as in the case of CO we would have a different situation, idealized in reaction [2]:

$$O\text{-}C\text{-}O_a + 2\,H_a \rightarrow [\,H\text{-}\underset{\displaystyle O}{\underset{|}{C}}\text{---}O\text{-}H\,]_a \rightarrow [H\text{-}\underset{\displaystyle O}{\underset{|}{C}}]_a + O\text{-}H_a \qquad [2]$$

If reaction [2] is valid, it is then a matter of the hydrogenation of the adsorbed oxygen species to produce the adsorbed intermediate (methanol) and its subsequent hydrogenation:

$$[H\text{-}C\text{-}O]_a + 3\,H_a \rightarrow [H_3C\text{-}O\text{-}H]_a + 2\,H_a \rightarrow CH_4 + H_2O \qquad [3]$$

Based on the carbon mass balance, about 75% of the hydrogenation of CO_2 would proceed by reaction [3] and the remainder would involve the breaking of the second C-O bond to continue along the normal FTS reaction pathway that is followed by CO hydrogenation. At this time, while the above mechanism accounts for the products that are produced from the hydrogenation of CO_2, it is very speculative. ^{14}C-tracer studies are planned that should provide some evidence to establish whether the speculation has merit.

The results to date for the hydrogenation of CO_2 indicate that it will not be commercially attractive using typical FTS catalysts based on iron or cobalt.

Acknowledgment

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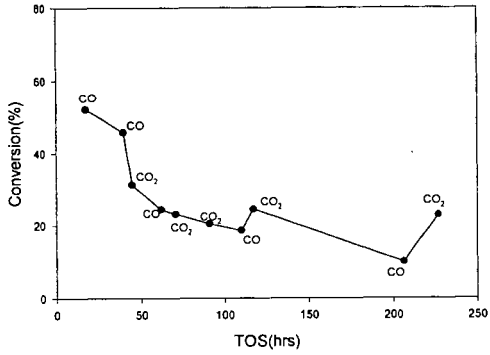

Fig.1 CO and CO_2 conversion as a function of time on stream

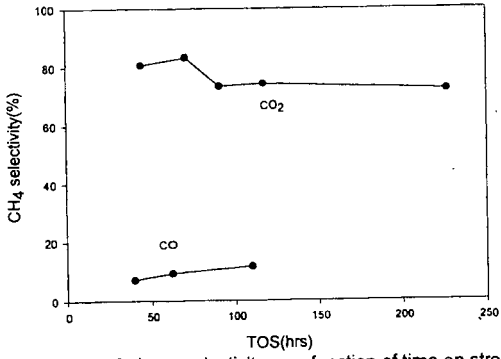

Fig. 2 Methane selectivity as a function of time on stream

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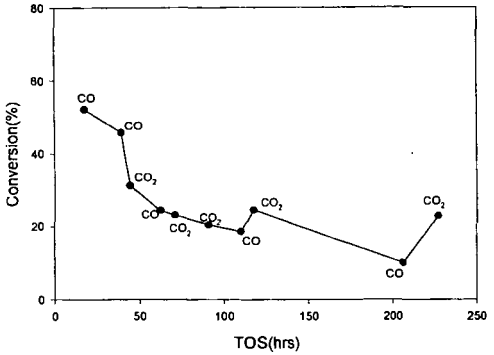

Fig.1 CO and CO_2 conversion as a function of time on stream

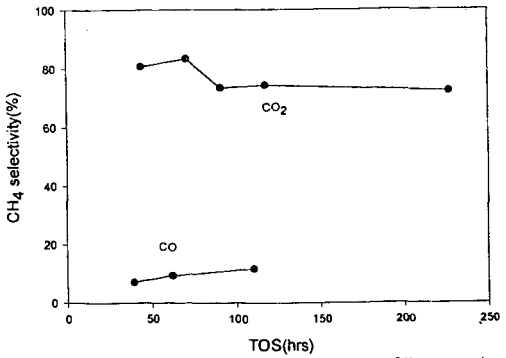

Fig. 2 Methane selectivity as a function of time on stream

OXIDATION OF SHORT CARBON FIBERS BY OXYGEN PLASMA

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INTRODUCTION

Oxidation of carbon fibers is a method commonly used to improve their adhesion to matrixes in the preparation of composite materials (1). The aim of this work is to evaluate the possibility and convenience of further increasing surface oxidation in short isotropic carbon fibers by the use of a cold oxygen plasma, not only in terms of the amount of oxygen introduced but also paying attention to the type of functionality achieved.

EXPERIMENTAL

Short, isotropic pitch carbon fibers, S-233 from Osaka Gas. Studied fibers include as supplied fibers plus two set of fibers submitted to oxygen plasma treatments of varying severity: 50W/1 min and 150 W / 5 min. All three sets of fibers (untreated and after oxygen plasma treatment) were characterized by C1s and O1s X-ray Photoelectron Spectroscopy (XPS, VG Scientific, Source : Al Mono Standard, CAE 20eV, Step 0.2 eV) (2) and by programmed pyrolytic degradation of oxygen complexes (TPD-MS).

RESULTS AND DISCUSSION

In Figure 1, XPS showed that the oxygen plasma treatment produces a strong surface oxidation. However, at higher power and longer time of exposure (150W/5min), the surface oxidative effect slightly declines. The same trend reversal due to a more drastic plasma treatment was already observed during oxidation of an activated carbon (3). Figure 2 shows a relative increase of the of –C=O and –C-O- region (<287 eV for C1s and < 533 eV for O1s) with increase of the treatment intensity.

TPD agrees with results obtained by XPS. CO_2 evolution showed a promotion of the acidic COO-functionality (carboxylic groups, anhydrides, lactones) in the fiber treated at 50 W / 1 min which recedes for the more severely treated fiber where basic surface groups become predominant.

CONCLUSIONS

XPS and TPD showed that oxygen plasma treatments increase the oxidation levels of short carbon fibers. This enrichment is compensated by a selective removal of the surface acidic groups on the most exposed surface. Different predominant functionalities can be achieved by varying the treatment conditions.

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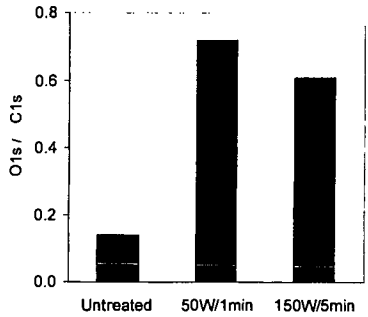

Figure 1. Effect of the plasma treatment on the XPS O1s / C1s ratio

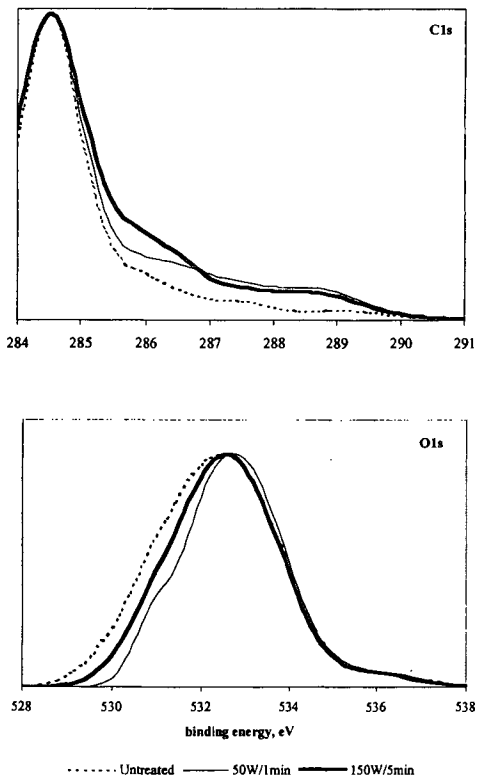

Figure 2 : Effect of the plasma treatment on the shape of the C1s and O1s spectra (normalized to the maximum of the untreated sample)

CARBON DEPOSITION ON Fe, Ni, AND Cr AND THEIR ALLOYS IN SUPERCRITICAL JET FUEL ENVIRONMENT

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Key words: carbon deposit, sulfur, jet fuel, Ni, Fe, Cr, SEM, TPO.

INTRODUCTION

The formation of carbon deposits on metal surface from decomposition of jet fuel is a major concern in the development of advanced aircraft in which the fuel is also used as a heat sink (1). Metal surface composition can strongly affect carbon deposition from thermally stressed jet fuel or model hydrocarbon (2). Carbon deposition on heat exchanger surfaces, filters, injectors and control valves can pose serious operational problems. Depending on the temperature and pressure of the system and the activity of metal surfaces, the deposition may be catalyzed by metal surfaces with the formation of filamentous carbon, or other forms of carbonaceous solids (3, 4).

A considerable volume of research has been carried out on Fe and Ni containing catalysts/or alloys over the past two to three decades to investigate their catalytic activity for the formation of carbonaceous deposits from various hydrocarbons under different conditions (5-7). Jet fuels may contain up to 2000 ppm sulfur that can have a significant effect on solid deposit formation from thermal stressing of fuels on metal surfaces. The effects of sulfur compounds on carbon deposition are not clear. Ohla and Grabke (8) reported that sulfur retarded graphitic carbon formation on iron, but the growth of graphitic carbon on nickel was accelerated by sulfur. Trimm and Turner (9) observed both the facilitation and retardation effect of sulfur on carbon deposition from a mixture of propane and hydrogen on pre-sulfided nickel, copper, iron and stainless steel surfaces. They suggested that the formation of stable metal sulfides on surfaces inhibit carbon deposition, whereas the formation, and subsequent decomposition of labile metal sulfides accelerated the deposition process.

The main objective of this study is to investigate and characterize the carbon and sulfur based solid deposit formation from jet fuel (JP-8) stressing on pure Ni, Fe and Cr and binary alloys of Fe/Ni (55/45), Fe/Ni (64/36) and Ni/Cr (80/20) surfaces.

EXPERIMENTAL

Thermal stressing of a JP-8 fuel (120 ppm constituent sulfur) was carried out in the presence of pure Ni, Fe, and Cr and Fe/Ni (55/45), Fe/Ni (64/36), and Ni/Cr (80/20) foil surfaces. The 15x0.3x0.01 cm coupons were placed at the bottom of a 20 cm, 0.63 cm (O.D) and 0.4 cm (I. D.) glass-lined tube reactor. The reaction system was heated to 500°C for 2 hours under argon flow at 500 psig prior to the introduction of the JP-8. Then, the preheated fuel at 250°C was introduced to the reactor. The reactor temperature and the fuel pressure were kept constant throughout the experiments at 500°C, and 500 psig, respectively. The flow rate of jet fuel was maintained at 4 ml/min. After 5 hours of stressing, the foils were cooled down under argon flow in the reaction system.

The stressed foils were analyzed using LECO-RC412 Multiphase Carbon analyzer to determine the total amount of carbon deposition on the foils as well as temperature programmed oxidation (TPO) burn-off profiles (10). In TPO experiments, the CO_2 evolution was measured by two IR cells as a function of time while heating the sample from 100°C to 900°C at a constant rate of 30°C/min under O_2 flowing at 750 ml/min. The carbon deposits were also examined by field emission SEM (FESEM), SEM with energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD).

RESULTS AND DISCUSSION

As shown in Table 1, the thermal stressing of JP-8 fuel on Ni and Fe and their alloys resulted in large amounts of carbonaceous solid deposits as compared to Cr and binary alloy with Ni, Ni/Cr (80/20). Total amounts of deposits were measured by using the LECO multi-phase carbon analyzer and the results were calculated in terms of μg of carbon per cm^2 surface area of the metal foil. The amount of carbon deposited on pure Ni, and Fe surfaces is 100, and 132 μg/cm^2,

respectively. The two binary alloys of Fe and Ni (with a relatively small difference in their bulk compositions) collected substantially different amounts of deposits. The alloy with 55% Fe and 45% Ni collected 55 $\mu g/cm^2$ carbon deposit (lower than that collected on pure Fe, or Ni), whereas 64% Fe and 36%Ni collected 389 $\mu g/cm^2$ (much higher than that collected on either pure metal surface). As expected, the addition of Cr to Ni reduced the deposit formation significantly. The binary Ni/Cr alloy collected 6 $\mu g/cm^2$ carbon deposit.

Table 1. The amount of carbon deposits collected on Ni, Fe, Fe/Ni (55/45), Fe/Ni (64/36), and Ni/Cr (80/20) surfaces. JP-8 was thermally stressed at 500°C and 500 psig for 5h at a flow rate of 4 ml/min.

Metal	Amount of deposit ($\mu g/cm^2$)
Ni	132
Fe	100
Fe/Ni (55/45)	55
Fe/Ni (64/36)	389
Ni/Cr (80/20)	6

Figure 1 shows the SEM micrographs of deposits formed from JP-8 stressing at 500°C on pure Ni, and Fe surfaces. In Figure 1a, it is seen that Ni surface is completely covered with filamentous deposits formed all over the surface. Most of the filaments have twisted shapes and they are longer than 5μm in length. High magnification images from FESEM examination showed that some of the filaments contain metal particles at their tips. An EDS elemental map analysis indicated that the surface contains high concentrations of sulfur in addition to carbon. The sulfur compounds present in jet fuel such as, thiophene and benzothiophene and their alkylated homologs appear to react with metal surfaces at high rates. An XRD analysis clearly showed the formation of Ni_3S_2 on the nickel surface upon stressing with JP-8.

The thermal stressing of JP-8 at 500°C on pure Fe surface produced two different sulfur-containing structures besides the carbon deposits. Figures 1b and 1c show hexagonal, tetragonal and monoclinic structures of $Fe_{1-x}S$, pyrrhotites, and FeS, troilite formed on pure Fe surface. In Figure 1b, a carbon deposit in amorphous form was also observed as bright overlayer between the sulfide crystals. There was no filamentous deposit observed on the Fe surface. The formation of highly crystalline sulfide structures may inhibit the catalytic effect of Fe surface to form carbon filaments. Trimm and Turner (9) also observed similar behavior during propane stressing in the presence of H_2S on the Fe surface. The authors reported that the Fe surface did not produce much carbon deposit when H_2S is present, but without H_2S, the Fe surface collected a significant amount of carbon deposit.

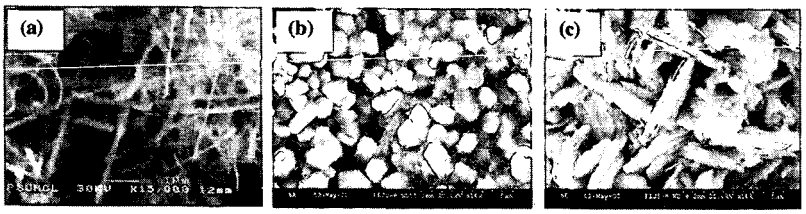

Figure 1. SEM micrographs of carbon deposits from thermal stressing of JP-8 at 500°C and 500 psig for 5h at flow rate of 4 ml/min on Ni (a), and Fe (b and c) surfaces.

Figures 2a, 2b and 2c show carbon and sulfur deposit structures on binary alloys of Fe/Ni (55/45), Fe/Ni (64/36) and Ni/Cr (80/20). No distinctive filamentous carbon morphology was observed on the surfaces of the deposited coupons. The deposits on the two Fe/Ni binary alloys appeared to have particulate morphologies with different surface coverage and particulate size. The bright carbon deposit structures seen on the Fe/Ni (55/45) surface in Figure 2a covered the whole alloy surface. The average particulate size of the deposits is 0.2 μm. However, on the Fe/Ni (64/36) shown in Figure 2b, deposits collected more on isolated areas without covering the surface completely. The average size of the particulate deposits is 0.5μm, larger than that observed on the other binary Fe/Ni alloy. From these observations and the TPO results, one can suggest that the Fe/Ni (64/36) alloy has a higher activity towards carbon deposition than the Fe/Ni (55/45) alloy. This difference in surface activity can be attributed to differences in surface composition and metallic phases present in these alloys among other factors, such as

impurities and physical characteristics of the alloy surfaces. Figure 2c shows that addition of Cr to Ni significantly reduced the surface activity towards sulfur and carbon corrosion. A relatively small amount of deposits observed on the surfaces consist of sulfide flakes and small particles of solid carbon.

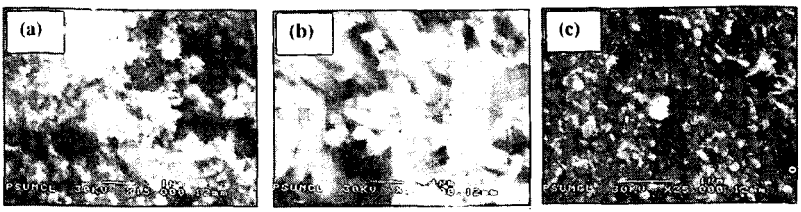

Figure 2. SEM micrographs of carbon deposits from thermal stressing of JP-8 at 500°C and 500 psig for 5h at flow rate of 4 ml/min on Fe/Ni (55/45)(a), Fe/Ni (64/36) (b) and Ni/Cr (80/20) (c) alloy surfaces.

The TPO profiles shown in Figure 3 indicate that on the pure Ni surface there are mainly two types of deposit structures that exhibit different reactivities in oxygen, giving two CO_2 evolution peaks centered at 375 and 750°C, respectively. The lower temperature peak can be attributed to reactive deposits, such as disordered, or amorphous deposits, and metal carbide (Ni_3C) particles. The higher temperature peak, on the other hand, should result from the oxidation of more ordered, e.g., graphitic, structures, produced around the metal particles in filamentous carbon structures.

On the Fe surface, three peaks were observed at 150, 275 and 450°C burn-off temperatures. The first low temperature peak can be related to the evaporation of trapped hydrocarbon molecules in the porous deposit structure, and the second broad peak results probably from the highly reactive carbon deposits formed between the sulfide crystals (Figure 1b). The third peak that appeared at around 450°C can be attributed to the oxidation of different iron carbides, e.g., Fe_5C_2, Fe_3C, and FeC, or of the more ordered carbon deposits formed on metal surfaces. No carbides were identified by XRD, probably because their quantity is very small compared to that of sulfides on the Fe surface.

The TPO profiles of the binary alloys of Fe and Ni are also shown in Figure 3. The heavy deposition on Fe/Ni (64/36) alloy is particularly noteworthy. The three major TPO peaks of the deposited alloys appeared at 150, 250-300 and 400°C. It is interesting that the high temperature peak (750°C) seen on the deposited nickel surface is absent on the deposited alloy surfaces. Similar to pure Fe TPO profiles, the first two peaks of alloys can be ascribed to the evaporation and oxidation of the trapped hydrocarbons, and the oxidation of the highly reactive solid deposits. The third very sharp peak at 400°C, probably results from the presence of an active alloy phase (Fe and Ni), which seems to catalyze the oxidation of the carbon deposits, as well.

As seen in Figure 2c, the amount of deposit on Ni/Cr alloy surface was very low compared to that obtained on Ni/Fe alloys. The TPO profile of the carbon deposits on Ni/Cr surface showed only one broad peak at 375°C that can be attributed to the oxidation of amorphous deposits and metallic carbides of Ni and Cr.

CONCLUSIONS

The catalytic effect of Ni and Fe surfaces resulted in significant amount of carbon deposits during the thermal stressing of JP-8 fuel in a flow reactor producing both filamentous, crystalline, amorphous, and metal carbide deposits. The sulfur compounds in the jet fuel lead to the formation of metal sulfides that cause surface corrosion and increase the surface area available for carbon deposition. The binary alloys of Fe and Ni further increased both carbon and sulfur deposition depending on the Fe content. The Cr addition to Ni, however, inhibited the catalytic activity of Ni significantly compared to the Ni and Fe alloys.

ACKNOWLEDGMENTS

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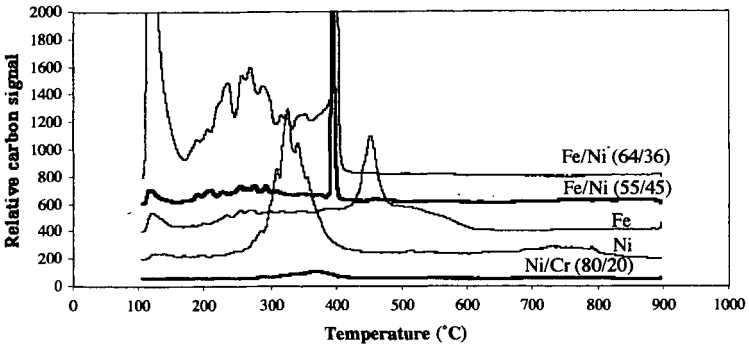

Figure 3. TPO profiles of deposits from JP-8 stressing at 500°C and 500 psig for 5h at a flow rate of 4 ml/min on pure Ni and Fe and Fe/Ni (55/45), Fe/Ni (64/36) and Ni/Cr (80/20) alloys.

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A LANDMARK PAPER ON CARBON-SUPPORTED CATALYSTS: THE REAL STORY REVEALED BY THE SCIENCE CITATION INDEX

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KEYWORDS: Carbon-supported catalysts, Carbon surface chemistry, Citation Index

INTRODUCTION

In the 1980's there was a resurgence of interest in understanding carbon as a catalyst support. It had been well documented by then that high catalyst dispersion can be achieved on carbon supports under certain conditions. This was attractive because it had also been established that carbon-supported hydrotreatment catalysts are much less prone to deactivation by coke deposition than the conventional alumina-supported catalysts. At Penn State, conditions were ideal to fully understand the virtues of carbon-supported catalysts and to rationalize the potential pitfalls in their preparation. Frank Derbyshire had just arrived from Mobil R&D and, being an expert in coal hydroprocessing, was eager to renew his studies on the catalytic properties of carbon. Alan Scaroni had been conducting an extensive study of coking propensities of carbon and alumina. And there was also the support of Phil Walker, with his encyclopedic knowledge of carbon materials and pioneering expertise in their use as catalyst supports.

Prior work had shown that "catalyst activity is strongly influenced by the interaction between the carbon surface and the deposited metal species" [1]. However, the exact nature of this influence was not clear [2]. Therefore, Derbyshire and his collaborators set out to "investigate the importance of surface functional groups on [sic] the activity of carbon-supported MoS_2 catalysts" [1]. In contrast to much of the previous work, in which "the carbons used ... were of different origin and varied in their chemical structure, textural properties and content of impurities," in this study "a single metal salt precursor and a single parent carbon were selected."

Offered below is a summary of the seminal importance of this study, even though its findings and conclusions, seen in hindsight, were somewhat ambiguous. While necessarily subjective, such an account is not only appropriate as a contribution to the symposium in memory of Frank Derbyshire but arguably also as a record of equal value (if not greater) as the more "objective" accounts offered by scientometricians or historians of science. Historians of science typically direct their efforts only at the "big stories," thus leaving us ignorant of the instructive historical context of "everyday science," where wheel reinventions are much more common. The Citation Index, an increasingly popular and potentially powerful tool, is too often used only by librarians and science administrators, as an end in itself rather than the means toward a more incisive analysis of the impact of a scientific publication.

HIGHLIGHTS OF "THE INFLUENCE OF SURFACE FUNCTIONALITY ON THE ACTIVITY OF CARBON-SUPPORTED CATALYSTS" [1]

Figure 1 reproduces the key results of this study. A "somewhat hydrophobic" polymer-derived carbon was subjected to widely varying oxidizing (a) and nitriding (b) treatments prior to their incipient wetness impregnation with ammonium heptamolybdate dissolved in a mixture of 90% H_2O/10% ethanol. Catalytic activity was determined at 450 °C by monitoring asphaltene conversion in batch hydrogenation tests of a process-derived coal liquefaction solvent. The extent of coke formation was determined by monitoring the weight gain of the catalyst after reaction. The effectiveness of carbon pretreatment was analyzed by elemental analysis and FT infrared spectroscopy. Maximum oxygen incorporation occurred when the carbon was treated in conc. HNO_3 and H_2SO_4 (ca. 25.3 and 20.1% O, respectively, vs. 1.4% in the parent carbon); nitrogen content increased from <0.05 to 0.53 and 0.87% after NH_3 treatment at 400 and 600 °C, respectively.

In contrast to the unclarified and largely detrimental effects of carbon oxidation, nitriding "was found to have a distinct effect in enhancing catalyst activity," and the authors proposed that this is because "nitrogen-containing surface groups ... provide preferential sites for the adsorption of Mo species." Even though the authors did not identify these sites, they argued prophetically that "the affinity between a particular carbon surface and the [selected catalyst] precursor will depend upon the compatibility of the two chemical structures."

IMPACT OF "THE INFLUENCE OF SURFACE FUNCTIONALITY ON THE ACTIVITY OF CARBON-SUPPORTED CATALYSTS" [1]

The story told by the Science Citation Index (Institute of Scientific Information, Philadelphia, PA), as of June 2000, is summarized in Figure 2. Not a widely cited paper, one would conclude, but such a conclusion would be a misleading one. As emphasized by Radovic and Rodríguez-Reinoso [2], this was the "first explicit attempt to clarify the influence of surface functional groups on the activity of carbon-supported catalysts." Intriguingly, however, most of the (non-self-) citing studies listed in Figure 2, even some of the most recent ones, do not identify it as such. Instead, the context of most citations is arguably peripheral and too often simply wrong.

(a) Inspired by Ref. 1, Guerrero-Ruiz et al. [3] performed a similar study of the role of nitrogen and oxygen surface groups in the behavior of carbon-supported iron and ruthenium CO hydrogenation catalysts, with ambiguous results.

(b) Abotsi and Scaroni [4-6] further pursued the issues raised in Ref. 1, emphasizing that "the activities of carbon-based catalysts are dependent on the nature and concentration of carbon surface functional groups." In particular, they were among the first investigators to appreciate [5] the crucial role of carbon surface charge [2]. Unfortunately, they mixed up the conditions of development of surface charge: it is the positively charged carbons, and not negatively charged ones (see p. 110 in Ref. [5]) that "are generally produced at high temperatures," and this turned out to be one of the keys to the preparation of highly dispersed molybdenum catalysts using anionic precursors [2, 7, 8].

(c) Groot et al. [9] echoed the underlying theme in Ref. 1, that chemical treatments should create catalyst anchoring sites on the support surface, and argued that "carbon blacks have a low density of functional (oxygen-containing) groups," which might serve as such sites.

(d) García and Schobert [10] mention Ref. 1 in passing, as a study of "hydrodesulfurization of thiophenes" [sic]. In a subsequent study by the same group [11], Ref. 1 is again miscited as a study in which, presumably, "limits [in achievable liquefaction conversion] have been observed beyond which further increases in Mo addition no longer have a significant effect."

(e) The study of Solar et al. [7] is a direct descendant of Ref. 1, and its success in providing some of the key answers regarding the role of carbon surface chemistry [2] was largely due to the fact that Ref. 1 had asked the right questions. The studies by Suh et al. [12], Martín-Gullón et al. [13], Kim et al. [14], Jansen and van Bekkum [15], Krishnankutty and Vannice [16], Bastl [17], Dandekar et al. [18], Vázquez et al. [19] and Aksoylu et al. [20] fall into the same category. In a recent study, de la Puente and coworkers [21, 22] revisited the topic of the interaction between Mo and activated carbons, did cite Ref. 1 in the appropriate context, but failed to recognize that the key issues had been largely resolved in the intervening period [2]. Disregarding the fact that adsorption of molybdate anions is suppressed by carbon oxidation, largely because of the presence of acidic functional groups (e.g., COOH), these authors concluded, rather paradoxically, that "acidic groups were acting as chemical anchorage centers." It is not clear how "oxygenated surface groups ... can act as chemical anchorage sites for molybdate ions." They argued that "[w]hen using incipient-wetness impregnation, electrostatic repulsions seem to be less important than other factors such as the hydrophilicity of the sample and the distribution of oxygen-containing surface groups;" they did not provide measurements of catalytic activity to support these interesting claims.

(f) Klinik and Grzybek [23] cite Ref. 1 as, presumably, a study which has shown that "the effect of oxidation [of carbon using concentrated HNO_3] depends on the structure of the starting material. A subsequent study by the same senior author [24] uses Ref. 1 to support the argument that "some bigger pores (macropores)" are formed during oxidation of an activated carbon.

(g) In what is perhaps the most intriguing one of all the inappropriate citations, Sakanishi et al. [25] invoke Ref. 1 after saying that "fine particles of a Mo-based catalyst are applied in a moving bed." Along the same lines, Mochida and Sakanishi [26] further invoke Ref. 1 in vain by saying that "titania and carbon have recently been examined as supports for iron and Ni-Mo sulfides."

Many other studies, especially in the 1990s, had as their *main* theme the effect of surface chemistry on the dispersion and activity of carbon-supported catalysts, and they are the ones that should have given, but did not, due credit to the pioneering effort of Derbyshire and his colleagues. Several examples will be provided during the presentation.

SUMMARY

Figure 3 is an attempt to synthesize our collective knowledge of the influence of surface functionality on the activity of carbon-supported catalysts. Its roots can be traced to the incisive questions posed by Frank Derbyshire and his colleagues in Ref. 1, as well as to improved understanding of "the compatibility of the two chemical structures" [1]. Apart from the effects of wetting and pore size distribution, carbon surface functionality governs the extent of adsorption of the catalyst precursor and the extent of its reduction or conversion to active state. Thus, for example, in catalyzing the oxygen transfer reactions illustrated here, the optimum surface chemistry is the one that (a) provides the anchoring sites for the catalyst precursor (e.g., carboxyl groups for ion exchange with cationic precursors), (b) allows favorable electrostatic interaction between the support and catalyst precursor (e.g., adsorption of anions at a pH less than the point of zero charge of the carbon), (c) prevents excessive catalyst mobility on the support surface, and (d) also facilitates the achievement of an intermediate oxidation state of the active phase, which in turn promotes oxygen transfer from the gas phase to the carbon surface.

The two-tiered value of the Science Citation Index to researchers, as opposed to librarians and research administrators, has been demonstrated here. On one hand it provides a quick start in the evaluation of scientific impact of a peer-reviewed publication. On the other hand, its increased use along the lines suggested here will hopefully force us all to be more careful, more selective and more responsible in collecting the lists of references for our publications. Perhaps sometime soon this important, yet too often neglected, activity will again be regarded as an opportunity to give credit where credit is really due and not as a matter of convenience, tradition and even nuisance. Had this been the case with Ref. 1, its "objective impact" would have been much closer to the admittedly subjective but arguably more appropriate evaluation presented here.

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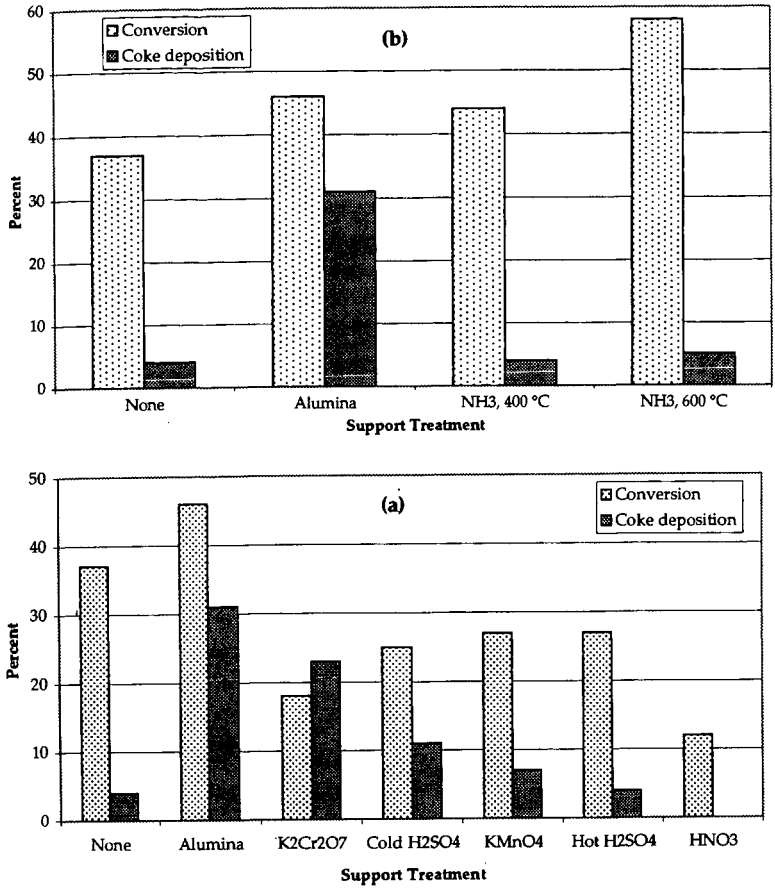

FIGURE 1. Effect of carbon surface functionality on the performance of sulfided Mo/C catalysts: (a) oxidative treatments; (b) nitriding treatments (from Ref. 1).

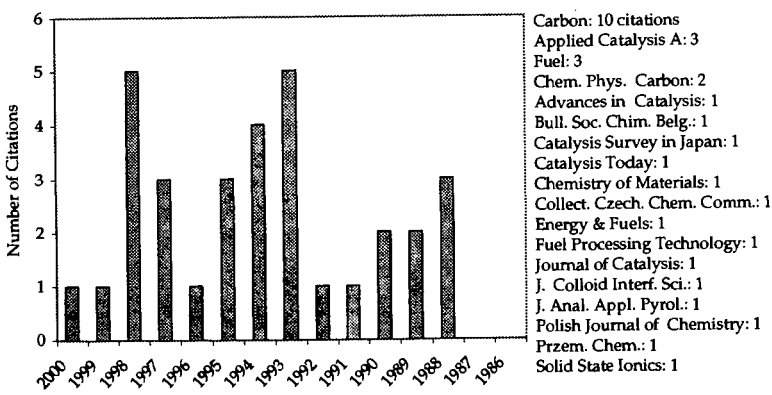

FIGURE 2. Summary of the Citation Index search for Ref. 1, as of June 2000.

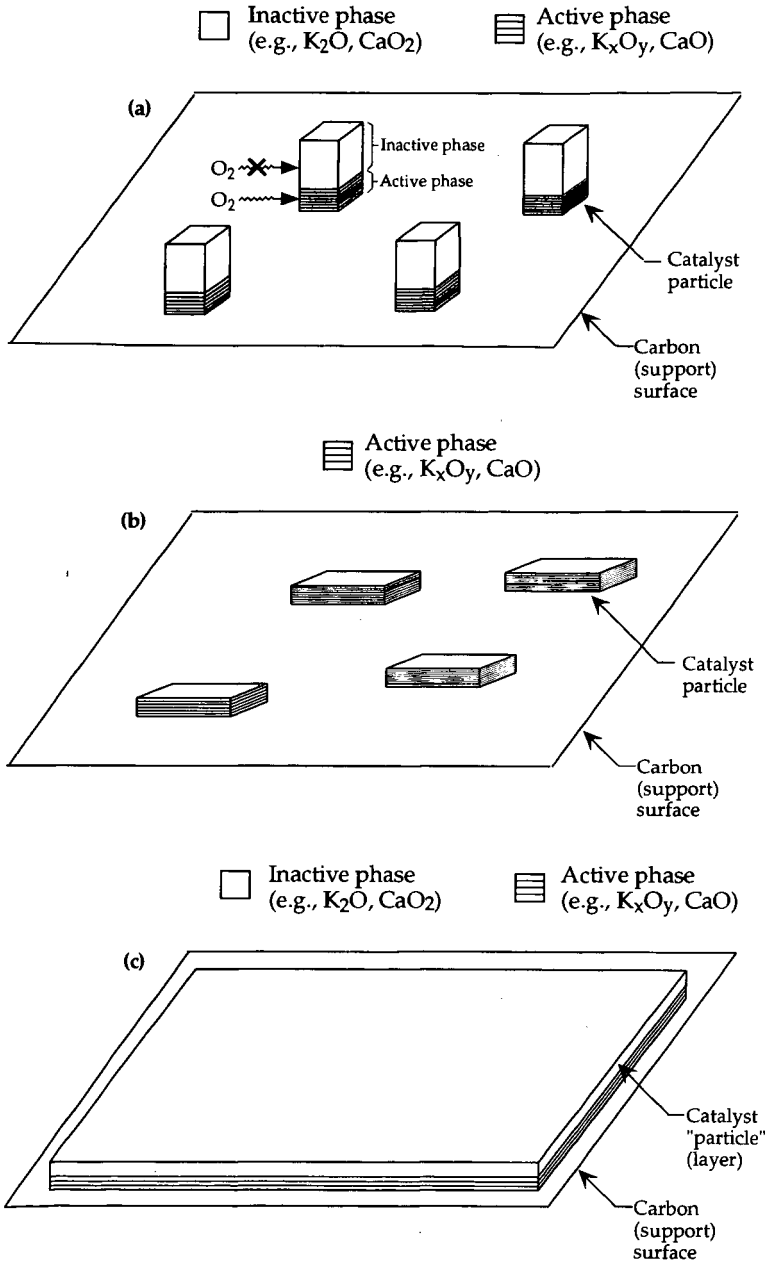

FIGURE 3. Summary of the influence of carbon surface functionality on the dispersion (and thus catalytic activity) of carbon-supported catalysts: (a) intermediate dispersion (activity); (b) high dispersion (activity); (c) low dispersion (activity).