

Preparation of Highly Dispersed NiMo Catalysts Supported on Carbon Black Particles of Hollow Spheres

Kinya Sakanishi, Haru-umi Hasuo, Isao Mochida, and Osamu Okuma^{†)}

Institute of Advanced Material Study, Kyushu University,
Kasuga, Fukuoka 816, Japan

^{†)} Polymer & Chemical Technology Lab., Kobe Steel, Ltd.,
Kobe, Hyogo 651-22, Japan

Abstract

One of unique carbon blacks, Ketjen Black(KB) which has extremely high surface area and low specific gravity, was selected as a catalyst support to prepare a highly dispersed NiMo catalyst for the hydrogenation of 1-methylnaphthalene(1-MN) using a magnetic-stirred autoclave of 50 ml capacity under the standard conditions of 380°C, 40 min, and 10 MPa H₂ reaction pressure. The catalyst, prepared from Mo dioxycetylacetonate (MoO₂-AA) and Ni(OAc)₂(Ni acetate) in their methanol solution by successive impregnations of Mo(10 wt%) and Ni(2 wt%), provided the highest conversion of 84 % to methyltetralins. Combinations of metal salts soluble in organic solvent, impregnation solvents, and surface properties of carbon black are suggested to be very important for the preparation of highly active catalysts. The nitric acid treatment introduced a large number of oxygen functional groups to the carbon black to improve the dispersion of water-soluble metal salts. It is also noted that KB-supported NiMo catalysts showed much higher activity for the present hydrogenation than a commercial NiMo/Al₂O₃.

Introduction

NiMo and CoMo catalysts supported on alumina extrudates have been extensively applied to the petroleum refineries as hydrotreating catalysts. Alumina is believed one of the best supports because it has large surface area for high dispersion of metals and high mechanical strength for the utilization to the conventional fixed bed flow-reactors. However, such alumina-supported Mo-based catalysts often suffer coking and plugging problems due to the acidity of alumina and the limited activity for the heavy polyaromatic hydrocarbons.¹⁻³⁾ Hence, recently Ca-modified NiMo/Al₂O₃ and fine particle Mo catalysts used in dispersed phase as well as the modified aluminas of controlled surface properties have been developed for the suppression of catalyst deactivation due to the coke formation.⁴⁻⁶⁾

Titania and carbon supports have attracted much attention for the preparation of anti-coking Mo-based catalysts because of their moderate polarity and metal dispersion ability⁷⁻¹⁰. Carbon supported catalysts can be recovered after the reactions by gravimetric separation due to their low specific gravity and hydrophobic properties for phase separation^{11,12}.

In the present study, Ketjen Black(KB), one of unique carbon blacks with extremely high surface area and low specific gravity, was selected as the support for NiMo. Ketjen Black(KB) particles have hollow spheric structure which brings about their extremely high surface area of ca. 1000 m²/g for high dispersion of active species and low specific gravity for catalyst recovery.¹³ Fine sphere without pore may be most suitable for the catalyst support for the heavy hydrocarbon. Carbon blacks have been reported to exhibit some catalytic activity for hydrocracking reaction due to its positively charged surface and high surface area with functional groups.^{14,15}

Such KB-supported NiMo catalysts are one of the most promising catalysts which have the fairly large activity for hydrogenation and liquefaction at the least amount of catalyst with the function for the recovery by gravimetric separation.

Experimental

Some properties of Ketjen Black(KB) ED and JD used in the present study are summarized in Table 1. Ni, Mo-supported KB catalysts (NiMo/KB) were prepared by impregnating methods using Ni(NO₃)₂ or Ni(OAc)₂ as Ni salts, and (NH₄)₆Mo₇O₂₄, Mo(CO)₆ or Mo dioxyacetylacetonate (MoO₂-AA) in water, methanol and their 9:1 mixture, or n-hexane according to the solubility of the salts. The catalyst precursors were dried at 120°C for 12 h in vacuo and presulfided in 5% H₂S/H₂ flow at 360°C for 3 h prior to the reactions. KB was pretreated in conc. nitric acid at 80°C for 1 h followed by filtration, repeated washing with water, and drying at 120°C in vacuo. The nitric acid-treated KB JD was abbreviated as KB JD-O, which was used for improved dispersion of metal species. A commercially available NiMo/Al₂O₃(KF-842) provided by Nippon Ketjen Co., was used for the comparison with the KB-supported NiMo catalysts.

1-Methylnaphthalene(1-MN; 1.0g), decalin(9.0g) and catalyst (5 wt% based on 1-MN) were charged into the autoclave of 50 ml capacity. Standard conditions for the hydrogenation were 380°C -40min and 10MPa H₂ of reaction pressure. The conversion to hydrogenated products of 1- and 5-methyltetralins and their selectivity were determined by GC and GC-MS to estimate the hydrogenation activity of the catalysts.

Results and Discussions

The hydrogenation activities of KB-supported NiMo catalysts are shown in Figure 1. KB JD which has a larger surface area of 1270 m²/g exhibited a little higher activity for 1-MN hydrogenation than KB EC(800 m²/g). The nitric acid-treated KB JD (KB JD-O) provided its supported NiMo catalyst with higher hydrogenation conversion of 60 %, increasing the selectivity to 1-methyltetralin (1-MT). The nitric acid treatment of carbon black introduced oxygen functional groups, improving the dispersion of metal salts on the carbon black support.

Figure 2 shows the effects of the species of Ni and Mo salts using KB JD support on the hydrogenation activity. The Mo species were very influential on the catalytic activity in combination with Ni(NO₃)₂ and KB JD support.

The combination of MoO₂-AA with Ni(NO₃)₂ in methanol solvent improved the hydrogenation conversion upto 82% ,suggesting that the balanced solubilities of Ni and Mo salts in impregnation solvent may be very important for preparing the highly dispersed NiMo catalyst on KB.

The activities of KB-supported NiMo catalyst are compared with a commercial NiMo/Al₂O₃ catalyst(KF-842) in Figure 3. The KB-supported NiMo catalyst of the highest activity, prepared from the successive impregnations of MoO₂-AA and Ni(OAc)₂ in methanol supported on KB JD, provided the 1-MN conversions of 84% and 47% respectively by the catalyst amounts of 5 wt%and 1%,respectively. On the other hand, powdered the commercial NiMo/Al₂O₃ (60mesh pass) exhibited a lower conversion when 5 wt% of the catalyst was applied. The reaction rates of KB-supported and commercial NiMo catalyst under conditions of 380°C ,10MPa H₂ reaction pressure by 1wt% catalyst amount are $v = 1.7949 \times 10^{-4}$ and 4.1287×10^{-5} , respectively. The KB catalyst has about 4.4 times more active than that of the commercial catalyst (see Figure 4).

Figures 5 and 6 show the effects of reaction pressure and temperature on 1-MN hydrogenation for NiMo/KB and KF-842. The KB-supported NiMo catalyst exhibited sharp increase of activity by increasing pressure to 7.0MPa H₂. Further increase of pressure increased moderately. In contrast , KF-842 did very moderate increase upto 10MPa.

The NiMo/KB showed significant activity at 320°C and increased its activity at higher temperature upto 360°C. Further higher temperature reduced the activity probable due to equilibrium limitation. KF-842required to show its significant activity.

Conclusion

KB supported NiMo was found very active for the hydrogenation of 1-methylnaphthalene, exceeding very much a commercial NiMo alumina catalyst of similar metal loading level. The activity at lower temperature and pressure should be noted.

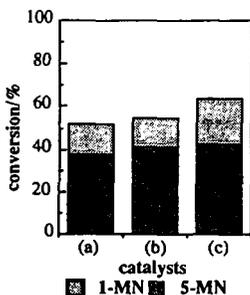
Kind and pretreatment of KB and supporting procedure were influential on the catalytic activity. The larger surface tends to give higher activity. The oxidation treatment was effective for the impregnation from the aqueous solution, while the impregnation from the organic solution gave the highest activity to the as-received KB with organic soluble salts of MoO₂-AA and Ni(OAc)₂.

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Table 1 Some properties of Ketjen Blacks

	KB EC	KB EC600JD
Surface area(m ² /g)	800	1270
Volatile matter(%)	0.5	0.7
pH	9.0	9.0
Particle size (nm)	30	30
Apparent density (g/l)	145	115
Ash (%)	0.1	0.1



Reaction conditions

Reaction temp.: 380°C
 Reaction press.: 10MPa
 Heating rate : 10°C/min
 catalyst : 5wt% (based on 1-MN, simultaneous impregnation from Ni(NO₃)₂ and (NH₄)₆Mo₇O₂₄)

catalysts support

- (a) KB EC
- (b) KB JD
- (c) KB JD-O

Fig.1 Effect of support species on 1-MN Hydrogenation(HYD).

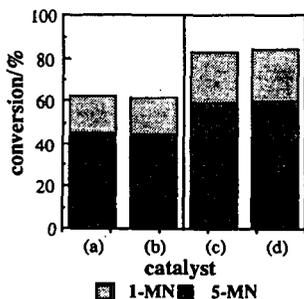


Fig.2 Effect of metal salts combination in organic solution on 1-MN HYD.

- metal salts**
- (a) Mo(CO)₆, Ni(NO₃)₂
 - (b) Mo(CO)₆, Ni(OAc)₂
 - (c) MoO₂-AA, Ni(NO₃)₂
 - (d) MoO₂-AA, Ni(OAc)₂

support : KB JD

successive impregnation in methanol

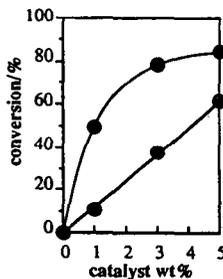
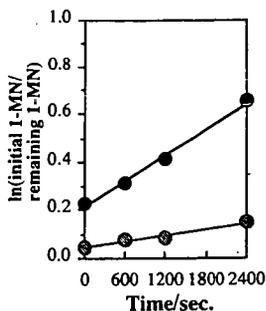


Fig.3 Effect of amount of catalysts on 1-MN HYD.

- KF-842 (60mesh under)
- Ni-Mo/KB JD (MoO₂-AA, Ni(OAc)₂)

(Other conditions are same as Fig. 1)



Reaction conditions

Reaction temp.: 380°C
 Reaction press.: 10MPa
 Heating rate : 10°C/min
 catalyst : 1wt%(based on 1-MN)

Ni-Mo/KB JD $\nu = 1.7949 \times 10^{-4}$
 KF-842 $\nu = 4.1287 \times 10^{-5}$

- KF-842 (60mesh under)
- Ni-Mo/KB JD (MoO₂-AA, Ni(OAc)₂)

Fig. 4 Comparison of commercial NiMo and KB-supported NiMo catalysts in the hydrogenation of 1-MN

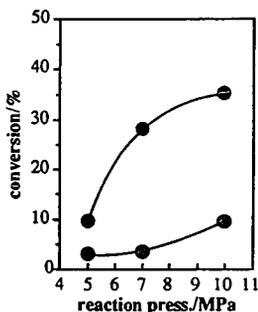


Fig.5 Effect of reaction pressure on 1-MN HYD.

- KF-842 (60mesh under)
 - Ni-Mo/KB JD (MoO₂-AA, Ni(OAc)₂)
- Reaction pressure : 5.0 ~ 10MPa
 Reaction Time : 40min

(Other conditions are same as Fig.4)

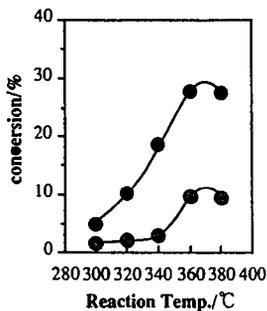


Fig. 6 Effect of reaction temperature on 1-MN HYD.

- KF-842 (60mesh under)
 - Ni-Mo/KB JD (MoO₂-AA, Ni(OAc)₂)
- Reaction temp.: 300~380°C
 Reaction time : 40min

(Other conditions are same as Fig.4)