CARBON SUPPORTED Ni-W SULFIDE CATALYSTS FOR HYDROPROCESSING DIESEL FEEDSTOCKS - DRAMATIC ACTIVITY IMPROVEMENT IN BY BORON PROMOTION

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Introduction

The adverse effect of the aromatics present in diesel fuel on the emissions, especially on the particulate emissions, has been well established. Mandated by the California Air Resources Board (CARB), the diesel fuel sold in California from October 1, 1993 was restricted to contain no more than 10% by volume of total aromatics. Diesel aromatics content is restricted in several European countries too.

Primarily two strategies are available for low aromatics diesel production. The first is to severely hydrotreat diesel feedstocks over commercial alumina supported Ni-Mo, Co-Mo or Ni-W catalysts at very high pressures. This brute force strategy suffers from several disadvantages including highly diminished throughput, and short catalyst lifetimes on stream, due to the low aromatics saturation activity of the commercial hydro-treating catalysts. The second strategy, which is a two stage process, is to severely hydrotreat the diesel feed-stocks in a first stage to very low sulfur and nitrogen contents of the order of only a few ppm, and then hydro-genate the desulfurized and denitrogenated oil over a noble metal catalyst. This strategy also suffers from several disadvantages including the need for two reactors in series with a gas separation step in between, and the high cost of the zeolite based noble metal catalysts.

Over the last two decades, there had been a tremendous interest in the application of carbon materials as catalyst supports [1-3], including their application for refinery hydroprocessing. For hydroprocessing, potential advantages of carbon supported catalysts over the commercial alumina supported catalysts include higher catalytic activities, easy metals recovery by burning off the carbon support, and low rates of deactivation. Due to their relatively inert nature, carbon supports are amenable to manipulation by various techniques, and carbon supported catalysts are significantly more responsive to small concentration of modifiers or promoters when compared to alumina supported catalysts.

We developed several *commercially viable* high activity carbon supported aromatics saturation catalysts for the production of low aromatics diesel by one-step hydrotreating. Some of these catalysts are 150-250% as active as the best of commercial hydrotreating catalysts, which translates to 1.5 to 2.5 times higher throughput using these catalysts. During our investigations, we discovered that by doping with small concentrations of boron, we could very significantly enhance the hydrodenitrogenation (HDN) and hydrodearomatization (HDAr) activities of carbon supported Ni-W catalysts [4]. However, the hydrodesulfurization (HDS) activity of the catalysts was improved only slightly by boron doping. The optimally boron doped Ni-W catalysts were almost twice as active for HDAr as the alumina supported Ni-W catalysts, and therefore have an excellent chance of finding commercial application for low aromatics diesel production.

Experimental

The feedstock for all our experiments was a light atmospheric gas oil (LAGO) containing 0.71 wt% sulfur, 500 wt ppm nitrogen, and 32% by wt of total aromatics. Its boiling range was 197 - 360°C.

Two activated carbon supports were used in our investigation. BX-7530, having a BET surface area of 1128 m^2/g, a nitrogen pore volume of 0.82 cc/g, and an ash content of less than 7 wt% was from Westvaco. It was ground to 20-40 mesh particles before catalyst preparation. Norit RX carbon had a BET surface area of 1474 m^2/g, a nitrogen pore volume of 0.67 cc/g, an extrudate diameter of 0.8 mm, and an ash content of less than 4 wt%.

Ammonium tetraborate, ammonium meta-tungstate, and nickel nitrate were used as the sources of B, W and Ni respectively. Incipient wetness impregnation by aqueous solutions of these salts was used to prepare all the catalysts. The catalysts were air dried at less than 150°C to eliminate the water.

The catalysts were presulfided in situ at 350°C by flowing 10% H_2S/H_2 before the diesel feedstock along with hydrogen was reacted over the catalyst in a continuous flow reactor system. The reaction was allowed to continue for at least 16 hours to reach steady state before samples were collected for analyses. Two sets of reaction conditions, (a) 340°C, 800 psig pressure, LHSV of 2, 2000 SCFB (standard cubic feet per barrel) of hydrogen (Condition 1), and (b) 385°C, 1500 psig pressure, LHSV of 2.5, 4000 SCFB of hydrogen (Condition 2), were employed to evaluate all the catalysts so that it is possible to obtain greater degree of discrimination between different catalysts. At Condition 1, the extent of HDAr was always less than 7%. At Condition 2, both HDS and HDN were close to 100%.

Results and Discussion

With BX-7530 carbon supported catalysts, the boron loading was varied between 0.0 and 1.7% by wt, at a fixed Ni and W loadings of 7.5% and 37% by wt respectively. The HDS and HDN results obtained at Condition 1 and the HDAr results obtained at Condition 2 are presented in Table 1.

Table 1: Effect of B on HDS, HDN, and HDAr Activities (Ni-W / BX-7530 Catalysts)

Wt% Boron in Catalyst	% HDS	Relative HDN Activity	Relative HDAr Activity
		Condition 1	Condition 2
0	88.5	1.00	1.00
0.20	91.5	1.09	1.62
0.41	90.5	0.92	1.30
0.86	89.5	1.00	1.73
1.30	**95.0**	**1.65**	**1.92**
1.70	92.3	1.28	1.54

It is clearly evident from the results presented in Table 1 that (a) with the BX-7530 carbon support, at the particular Ni and W loadings employed, the optimum B concentration for maximum HDS, HDN, and HDAr activities seems to be about 1.3 wt%, and (b) the optimally B doped catalyst was 65% more active for HDN, and was almost twice as active for HDAr than the catalyst with no B added. This is the first observation of its kind in the world, and this magnitude of HDN and HDAr activity improvements at such low level of B loading are completely unexpected and are remarkable.

Table 2 presents the HDAr results obtained with Norit RX carbon based Ni-W catalysts. The Ni and W loadings were maintained at 6 wt% and 36 wt% respectively, and the B loading was varied between 0.0 and 1.2 wt%.

Table 2: Effect of B on HDAr activity (Norit RX carbon supported Ni-W catalysts)

Wt% Boron in Catalyst	Relative HDAr activity
0	1.00
0.40	**1.50**
0.80	1.25
1.20	1.21

Comparing the results in Table 2 with those in Table 1, the following observations can be made:
(a) With Ni-W / Norit RX catalysts, maximum activity was obtained at 0.4 wt% B, compared to the 1.3 wt% B required for the BX-7530 supported catalysts, and (b) the maximum improvement in the HDAr activity by B promotion, of the Ni-W / Norit RX catalyst was only 50% as against the 92% with the BX-7530 carbon supported catalyst.

There are several possible mechanisms through which B can improve the catalytic activities of the Ni-W / Carbon catalysts. Increasing the catalyst acidity, improving the active metal sulfide dispersion, inducing larger non-stoichiometry in the metal sulfide phase, and increasing the concentration of the "Ni-W-S" active phase on the catalyst surface are some of these possibilities. Further investigation is necessary to understand the exact mechanism(s) through which B improves the catalytic activities of the carbon supported Ni-W catalysts.

References

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