Novel Ni-ZnO-Al_2O_3 Nanowire Catalysts for Hydro-desulfurization of Diesel

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Introduction

Reduction of sulfur in diesel fuel is an important means for improving air quality because of the negative impact sulfur has on the performance of automotive engine exhaust inhibitors. Sulfur irreversibly poisons noble metal catalysts present in the converter of an engine, which causes an increase in incomplete combustion species in the exhaust. Low sulfur concentrations are desirable from an operational standpoint for refineries because even trace amounts of sulfur can deactivate the noble metal catalysts irreversibly. The conventional hydro-desulfurization (HDS) process utilizes alumina- and silica-supported cobalt or nickel molybdenum catalysts. However, sulfur levels after conventional HDS treatment are still too high for these downstream sulfur-sensitive applications. Most of the "benign" non-cyclic sulfur compounds can be dealt with conventional HDS. The challenging compounds are thiophenes and benzo-thiophenes which are difficult to remove due to their aromaticity and consequent low reactivity [1-2].

Therefore, novel catalysts with high performance toward ultra-deep desulfurization of diesel, are needed. Here, we demonstrate the feasibility of nickel nanoparticles supported on zinc oxide nanowires to clean off difficult thiophenic compounds for prolonged time periods. Nickel catalyzes hydrogenation as well as the cleaving of cyclic sulfur compounds like thiophenes. During conventional hydrogenation and HDS, active Ni sites get continually sulfided (NiS) thereby extinguishing all catalytic activity eventually. To tackle this problem, we are proposing the concept of reactive adsorption, using ZnO as a support, to maintain a steady fraction of active nickel surface sites for deep desulfurization [3-4]. In this concept, the catalytic activity can be extended until all ZnO is completely converted to ZnS.

Materials and Methods

ZnO nanowires were produced by our group using an atmospheric plasma jet based reactor described elsewhere [5]. Nickel was loaded onto ZnO NW and γ-alumina. The Ni-ZnO-Al2O3 dough was extruded and calcined at 400 °C for 2 h. Desulfurization studies were carried out in a packed bed reactor using a standard diesel feed acquired from Exxon containing 25% of various aromatic and poly-aromatic compounds, and 20 ppm thiophenic sulfur. The catalyst was characterized using techniques such as TPR, BET, XRD, SEM, and TEM.

Results and Discussion

The catalyst composition is shown in Table 1.

Table 1. Catalyst composition

Catalyst	%Ni	%ZnO nanowires	% Al2O3
	15	65	20

The treated diesel samples taken at various on-stream intervals were found to be promising, i.e. ultra-deep desulfurization with ultra low sulfur over a 12 h period. Figure 7 (a) shows the photographs of treated diesel as a function of time. The sulfur uptake capacity of the Ni/ZnO NW/Al2O3 catalyst looks encouraging (Fig. 7 (b)). The TEM analysis of the spent catalyst indicated that there was selective coking of the catalyst. Suboptimal operating conditions and the high aromatics content in the diesel feed resulted in such coking. Increasing temperature and hydrogen pressure will help reduce such coking when using our highly active catalyst. Deep desulfurization activity of our catalyst with a low feed aromatics content is expected to yield zero sulfur over a long period of time [6]. Research is ongoing to increase the lifetime of catalysts.

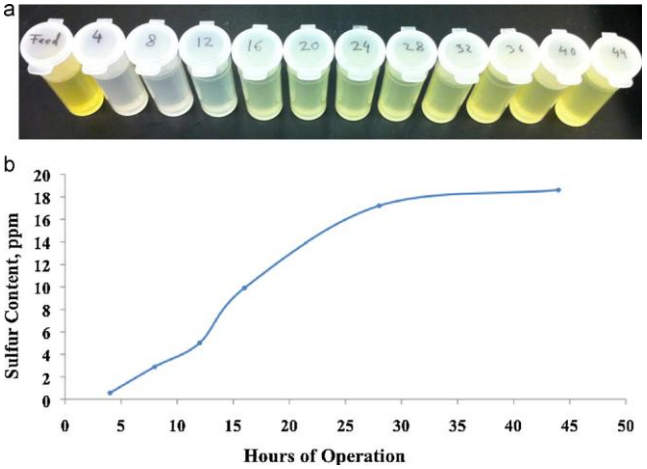

Figure 1. Desulfurization test results: (a) photographs of diesel samples taken at various times on stream; and (b) the quantification of sulfur content in the treated diesel.

Significance

The catalytic system demonstrated here can be applied for deep desulfurization of a wide variety of fuels such as naphtha, kerosene, and heavier oils.

References

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