"Nanowire catalysts for ultra-deep hydro-desulfurization and aromatic hydrogenation"

M. Gupta [a,b,1], J. He [a], T. Nguyen [b], F. Petzold [b], D. Fonseca [a], J.B. Jasinski [b], M.K. Sunkara [a,b,*]

[a] Advanced Energy Materials, LLC, USA
[b] Conn Center for Renewable Energy Research, University of Louisville, Louisville, KY 40292, USA

A B S T R A C T

Here, we report high performance catalysts designed using nanowire supports. Specifically, nickel clusters supported on Zinc Oxide (ZnO) nanowires and γ-alumina found to be highly active for ultra-deep desulfurization and aromatic hydrogenation of diesel. They were also found to be highly active for ultra-deep desulfurization of gasoline and kerosene. The catalysts reduced sulfur from diesel, gasoline, and kerosene fuels containing sulfur as high as approximately 200 ppm to less than 1 ppm with sustained activity over testing periods of 100–150 h. The feed contained some of the most difficult to remove sulfur compounds such as 4-methyldibenzothiophene (MDBT), 4,6-dimethyldibenzothiophene (DMDBT). In addition to activity towards ultra-deep desulfurization, these catalysts have shown to be active towards saturate/hydrogenate aromatics in diesel at moderate reaction conditions (30 bar, 290 °C, and LHSV 2.2 h^{-1}). The active catalytic site was determined to be a super Ni rich Ni_xZn_y phase which seemed to remain essentially sulfur free during the reaction. The regenerated catalyst showed reasonable activity toward desulfurization of gasoline.

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1. Introduction

Reduction of sulfur in diesel fuel is important for the environment as well as for the performance of catalytic converter in an automobile. Sulfur compounds in the fuels contribute to emissions of SO_2 and sulfate particulate matter. Sulfur in transportation fuels degrades the catalytic converter resulting in increased NO_x and SO_x emissions which increase the potential for causing acid rain. Sulfur must be removed in any catalytic process because it poisons/deactivates the catalyst [1], which otherwise require frequent regeneration or replacement. Likewise, the performance of other catalytic devices such as fuel cells is also extremely sensitive to the presence of sulfur [2].

As of September 2007, all on-highway diesel fuel (ultra-low-sulfur diesel (ULSD)) sold at gas stations in the United States contains less than 15 ppm of sulfur. The demand for ULSD has increased significantly in the last few years [3] because of continual reduction in sulfur limits in transportation fuels. As far as

the gasoline is concerned, the Environmental Protection Agency (EPA) proposed a new regulation recently that would reduce its current sulfur content from 30 ppm to 10 ppm by 2017 [4] and much stricter limits are anticipated in future. Therefore, refiners in the United States and Europe have installed numerous new middle distillate hydrotreaters or revamped existing facilities. Governments in developing countries such as India, Mexico, and China are also imposing low sulfur regulations which has increased the demand for ultra-deep desulfurization catalysts around the world [5].

Diesel and gasoline fuels contain a variety of heterocyclic sulfur compounds at few tens of ppm level which are difficult to remove using traditional hydro-sulfurization catalyst used today. For example, many catalysts undergo steric hindrance effects during adsorption with species such as 4-substituted and 4,6-disubstituted dibenzothiophenes. The refractory nature of b-DBTs comes from the steric hindrance around the sulfur atom [3,6]. The removal of these latter compounds presents a significant challenge to the industry [7–10]. The conventional hydro-desulfurization (HDS) process utilizes alumina- and silica-supported cobalt or nickel molybdenum catalyst and operate at 350–390 °C, and pressures between 60 and 90 bars [5]. Currently, for ultra-low sulfur diesel (ULSD) production, hydrotreating catalysts include nickel–molybdenum–sulfur (Ni–Mo–S) or cobalt–molybdenum–sulfur (Co–Mo–S) supported on γ-alumina

(Al$_2$O$_3$) [3]. However, the above catalysts suffer from low activity for heterocyclic compounds present below 50 ppm and require higher temperature and pressure and/or low space velocities to bring sulfur down below 15 ppm [11,12]. At higher temperatures, there are some inherent issues that reduce the catalyst activity, and they include carbon deposition on catalyst surface and change of catalyst surface itself (re-organization of surface) [12,13]. Hence, there is a crucial need to design high activity catalysts for ultra-deep desulfurization at moderate process conditions. Moreover, the presence of sulfur even at few ppm level can pose significant problems with hydrogen production via diesel reforming for fuel cell applications [14].

Aromatic hydrogenation is also critical for the improvement of fuel quality. Reduction in aromatics improves cetane number thus improves the fuel quality. High aromatic content in diesel results in low cetane number and therefore more NO$_x$ emissions and particulates from diesel and un-combusted hydrocarbon emissions [15]. Hence, it is highly critical to reduce aromatics level in fuel to make it environmentally friendly as well as better fuel quality. For example, Cooper et al. [15] found that when the aromatic content was 37%, the cetane number was 37 for a diesel fuel. The cetane number increased to 48 when aromatic content in diesel was decreased to 20%. Aromatics affect the formation of particulate and polycyclic aromatic hydrocarbons (PAH) emission. A high aromatic content results in a high flame temperature and a low cetane number, which increases NO$_x$ emissions [15]. Also, because aromatics are considered carcinogens, they are regulated to no more than 35% by volume (or 20% by wt) for ULSD. Therefore, a reduction in aromatics is good for both fuel quality and the environment.

Different feed-stocks contain different amounts of aromatics. For example, straight run gas oils usually contain 25–30% total aromatics, whereas cracked distillates – e.g., light cycle oil (LCO) or coker gas oil (CGO) contain 50–75% total aromatics [3]. The industry uses a two-step process: (1) a partial hydrogenation of aromatics on conventional NiMo/Al$_2$O$_3$ or CoMo/Al$_2$O$_3$ sulfide catalysts, and then (2) deep hydrogenation on supported noble metal (Pt or Pd; Pd–Pt) catalysts with improved sulfur tolerance [15,16]. Recently, there has been some progress towards one-stage processes [17]. The challenge with catalyst design is that hydrogenation of aromatics takes place during the deep desulfurization of diesel [18]. Therefore, the catalysts need to be highly active towards hydrogenation in the presence of heterocyclic sulfur compounds.

Here, we show the feasibility of using nickel nanoparticles supported on zinc oxide nanowire surfaces as catalysts. Nickel can catalyze the hydrogenation reaction as well as the cleaving of cyclic sulfur compounds like thiophenes. The use of ZnO follows that of reactive adsorption concept in which sulfur from Ni clusters transfer to ZnO nanowire support [19–23]. Tawara's group [20] was the first to report the performance of a Ni/ZnO catalyst as an adsorptive HDS catalyst for the kerosene toward kerosene-fed fuel cell applications. Active nickel sites could be maintained until the ZnO nanowire supports get sulfided fully. ConocoPhillips developed a sulfur removal technology for gasoline, based on reactive adsorption [24].

The use of nanowire support has multi-fold advantages for catalyst design. Some of them are highlighted here: (1) the single crystal nature and faceting improves the properties of the supported catalytically-active metals through the resulting nickel cluster morphology; (2) ability to produce well-defined surface facets therefore higher concentration of desired sites [25]; (2) potentially enhance metal-support interactions; (3) nanowire support undergo less sintering than conventional supports [26,27]; and (4) nanoparticle on nanowire morphology presents an easier diffusion pathway for sulfur transfer from supported clusters to underlying support to maintain a high surface concentration of active nickel sites for deep desulfurization activity.
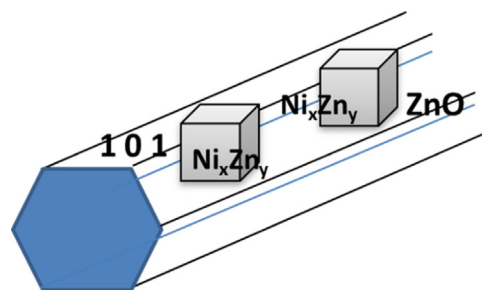

Fig. 1. A schematic showing uniform morphologies for nanoclusters produced on mono-crystalline facets of c-plane oriented ZnO nanowire.

Even though the nanowire supports are predicted to have the above-mentioned advantages, there are no studies for both deep HDS and aromatic hydrogenation using catalysts made from nanowire powders. Here, we report the ultra-deep HDS activity of nickel-rich metal cluster supported on ZnO NWs (Fig. 1). The activity is tested using a variety of fuels and most importantly with diesel that contains one of the most-refractive sulfur compounds, 4,6-Dimethyldibenzothiophene (DMDBT). The nature of active catalyst clusters, uniformity of morphology, morphological stability, and activity of fresh and regenerated catalysts, are of fundamental interest.

2. Experimental

2.1. Catalyst preparation

Several catalyst samples with varying compositions of Ni on ZnO nanowires with and without alumina were prepared. General method used for preparing these catalysts is as follows: ZnO nanowires were produced using an atmospheric plasma jet based reactor described elsewhere [28]. ZnO nanowires were purified to remove ZnO/Zn micro and nanoparticles. A mixture of deionized (DI) water and nanowires was made and sonicated for 10 min and then left to settle for 10 min. The unwanted material quickly settles down in the beaker. The ZnO NW suspensions were decanted into another beaker. Then NH$_4$OH was added to the suspension to make pH 9.2 (iso-electric point of ZnO NW). Nanowires settle down in a few minutes and then the water was decanted to obtain "pure" ZnO NW. These purified nanowires were then used to prepare catalyst.

A slurry was made by adding DI water to purified ZnO NW and γ-Al$_2$O$_3$. Aqueous solutions of nickel acetate (NiCOOH·2H$_2$O) was made by adding DI water and by heating and stirring the solution at 90 °C. The nickel acetate solution was added drop-by-drop to the slurry while the mixture being stirred. The pH was maintained around 9.0 by adding aqueous solution of NH$_4$OH. Then, the mixture was dried at 80 °C for 15 h in a furnace and stirred once during drying. Thereafter, the mixture was dried at 150 °C for a few hours and stirred once to obtain a thick paste for extrusion. Thereafter, the paste was extruded and dried at 150 °C for 1 h. Finally, they were calcined at 390 °C for 2–2.5 h. A batch of extrudates used in this work is shown in Fig. 2. The length and diameter of these extrudates were 4–5 mm and 1–1.5 mm, respectively. These extrudates were then used for the hydro-desulfurization and aromatic hydrogenation tests. With the addition of molybdenyl acetylacetonate, the Ni and Mo supported on ZnO NW catalyst was also prepared using the same synthesis method.

2.2. Ultra-deep desulfurization

First, the catalyst was reduced at 430 °C for 3 h with a H$_2$ flow rate of 0.15 L/min at atmospheric pressure. The hydro-desulfurization reaction was carried out at 30 bar and 290 °C