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A Parallel Colorimetric Method for the Rapid Discovery and Optimization of Heterogeneous Hydrodesulfurization Catalysts

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Combinatorial and highly parallel methods for heterogeneous catalyst discovery are quickly gaining importance to supplement traditional methods for evaluating catalyst design and activity.[1−6] The ability to determine the activity of a series of catalysts in a chemical process *simultaneously* allows one to quickly identify and optimize the most active catalyst compositions and conditions. In this Communication, we report a colorimetric method to rapidly screen heterogeneous catalysts for activity in the hydrodesulfurization (HDS) of petroleum feedstocks. The relatively severe temperatures (>250 °C) and pressures (>2500 kPa) required for HDS called for a unique set of experimental criteria for the screen to function properly.

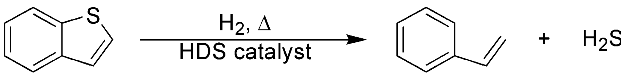
HDS is a high temperature and pressure catalytic process to remove sulfur from hydrocarbons.[7] Sulfur-containing compounds such as benzothiophenes are reacted with hydrogen in the presence of an HDS catalyst to generate the corresponding desulfurized hydrocarbon and H_2S (Scheme 1). The oil industry relies heavily on this process to lower the amount of sulfur in petroleum feedstocks.[7] Environmental and health concerns over SO_x emissions from the combustion of fossil fuels has forced oil refiners to dramatically reduce the sulfur content in gasoline and diesel fuels.[8] The increased need for ultraclean fuels has prompted new research into more efficient HDS catalysts.[9] While current HDS catalysts are extraordinarily efficient at removing low molecular weight sulfides and thiophenes, higher molecular weight sulfur compounds (i.e., α-substituted dibenzothiophenes) resist reductive desulfurization.[10]

Our highly parallel method for HDS catalyst evaluation utilizes an optical change in a dye molecule to signal HDS activity. An optical approach offers the advantage of avoiding laborious analytical methods by simply being able to visually determine activity or by employing facile absorbance/fluorescence methods. Recently, the use of this reactive dye strategy to screen catalysts for hydrosilylation,[11] the Heck reaction,[12] and electrocatalysts[13] for fuel cell applications has been described.

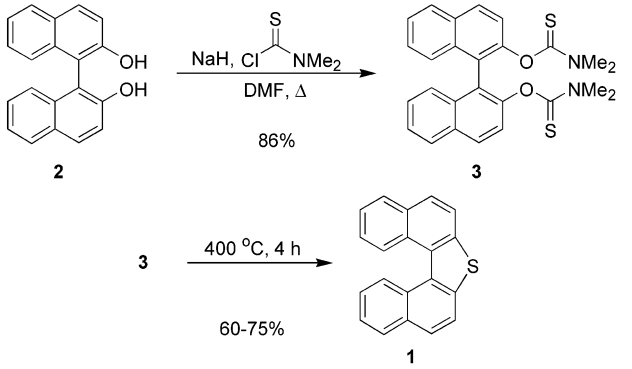
The design of dye molecules used to probe catalyst activity should mimic the sulfur compounds that are more difficult to treat by current HDS catalysts. In addition, the dye molecule needs to meet an additional set of criteria to cope with high temperatures (>250 °C) and pressures (>2500 kPa) used for HDS. This includes low volatility to avoid cross talk between sample cells exposed to a common set of reaction conditions. The dye molecule should be thermally stable under the HDS conditions to avoid false positives from decomposition events. Also, the HDS products should not interfere with the optical response of the dye molecule to make analysis unambiguous.

A molecule we envisioned to fit the above requirements for the HDS screen was 1,1′-binaphthothiophene **1**. This compound is readily available in two steps from BINOL **2** (Scheme 2).[14] BINOL **2** was deprotonated with NaH and reacted with dimethylthiocarbamoyl chloride to give intermediate bisthiocarbamate **3** in 86% yield. Thermal rearrangement and subsequent intramolecular displacement of bisthiocarbamate **3** at 400 °C gave thiophene **1** in 60−75% yield after SiO_2 chromatography and crystallization.

Scheme 1. Hydrodesulfurization of Benzothiophene



Scheme 2. Synthesis of Binaphthothiophene **1**



The spectral properties of thiophene **1** and its major HDS product, binaphthyl **4**, are shown in Figure 1. The sulfur group in **1** constrains the conformation of the binaphthyl ring to an approximate planar geometry and imparts extended conjugation between the naphthyl rings. Absorbance maxima can be observed at 353, 337, 313, 301, 276, and 236 nm by UV−vis spectroscopy in solution. The absorption profile for the major HDS product, binaphthyl **4**, shows absorbance maxima at 293 and 283 nm and is optically transparent beyond 330 nm. Therefore, the absorbance maxima at 353 nm for thiophene **1** allows assessment of HDS catalyst activity without interference from those HDS products which absorb in the long UV−vis region.

Thiophene **1** was evaluated as a parallel screen for catalyst activity using two known HDS catalysts (Table 1, entries 1−2) and four noncatalysts (entries 3−6) expected to be inactive under reaction conditions. The noncatalysts chosen are typical of solid supports used for heterogeneous catalysis. A control or blank with no catalyst (entry 7) was also used. To each reaction well (an open 1 dram glass vial) were added ~30 mg of catalyst and a decalin solution of thiophene **1** (2.00 mL, 5.0×10^{-5} M). All of the catalyst solutions were bundled together and loaded into the same pressure reactor. The void space inside the reactor was filled with decalin to a level equal to that of the solution in the vials. The reactor was sealed and charged with H_2 and subjected to standard HDS

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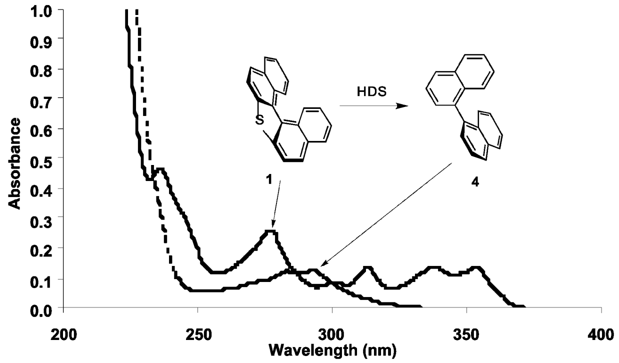

Figure 1. UV−vis absorption spectra of thiophene **1** (9.4×10^{-6} M, solid line) and binaphthyl **4** (9.0×10^{-6} M, dashed line) in decalin.

Table 1. Average Percentage of Thiophene **1** Consumed during HDS from Four Runs

entry	catalyst	% thiophene **1** consumed[a]
1	Ni/Mo on alumina[b]	98.0 ± 0.8
2	Co/Mo on alumina[b]	95.8 ± 5.5
3	activated charcoal	99.4 ± 0.9
4	alumina	35.2 ± 8.8
5	silica gel	20.0 ± 6.8
6	4 Å molecular sieves	11.8 ± 3.2
7	no catalyst	−0.7 ± 2.1

[a] Quantified from the absorbance at 353 nm using Beer's law ($\epsilon = 14\,400$ cm^{-1} M^{-1}). [b] Ni/Mo catalyst contained 9 wt % NiO and 32 wt % MoO_3 balanced with Al_2O_3. Co/Mo catalyst contained 5 wt % CoO and 10 wt % MoO_3 balanced with Al_2O_3. Weight percentages determined by electron microprobe.

conditions (300 °C at 5066 kPa). After these conditions were maintained for 4 h, the reactor was cooled to room temperature and each solution subjected to UV−vis analysis to evaluate catalyst activity. Since some solvent in each vial was lost to evaporation during the reaction, the contents of each vial were diluted to a uniform volume to permit quantitative spectrophotometric measurements.

The HDS parallel catalyst screening using thiophene **1** under the conditions described above is summarized in Table 1. Each entry in Table 1 represents the average percentage of thiophene **1** consumed in four separate runs by a catalyst. As expected, the known HDS catalysts, Ni/Mo and Co/Mo on alumina (entries 1 and 2), were shown to have consumed nearly 100% of the dye molecule. The standard deviation for the amount of thiophene **1** consumed for each catalyst was small, indicating the HDS catalyst screen was very reproducible from run to run. The vial containing no catalyst (entry 7) showed no change in absorption profile, indicating there was no cross talk of the dye between other vials in the reactor. A control study using only decalin solutions of thiophene **1** and decalin also confirmed the absence of dye migration. However, cross talk of the major HDS product binaphthyl **4** was observed by MS. While this precludes direct analysis of the HDS products for each catalyst under the conditions used in this study, its presence in the other vials does not interfere with the screen for catalyst activity if monitored as consumption of thiophene **1**. Further refinement of the procedure by using higher boiling solvents or lower HDS reaction temperatures or a modified reactor design may very well eliminate migration of the solvent and HDS products. Not too surprisingly, the dye had completely disappeared from the solution containing the adsorbent, activated charcoal (entry 3). Activated charcoal is known to have a high capacity for adsorbing thiophenes.[15,16] In addition, this false positive could also be discarded as a possible HDS catalyst by running a bulk reaction and looking for HDS products by MS. The other noncatalysts (entries 4−6), alumina, silica gel, and 4 Å molecular sieves, also absorbed the dye to varying but much lesser degrees, as absorption bands for thiophene **1** were still observed. Adsorption effects on screening should be readily minimized through the use of higher concentrations of **1**.

This highly parallel method based on the change in optical properties of binaphthothiophene **1** allows for the rapid and facile screening of a variety of potential HDS catalysts simultaneously. The dye should also be a useful diagnostic for individual catalyst performance in more traditional and larger scale HDS experiments. Both applications should result in greater productivity in the discovery of more reactive catalysts for HDS processing of fuels. Presently, we are developing derivatives of **1** with added alkyl substituents to increase the steric environment around the sulfur. This less reactive screening dye should make it possible to detect subtle differences in catalyst activity and identify catalysts that will more effectively remove sulfur from similarly adorned benzothiophenes, the most resistant repositories of sulfur in petroleum-based fuels. Furthermore, one could potentially apply this type of colorimetric screen to assist with the discovery and optimization of other catalytic systems such as hydrodenitrogenation and dearomatization.

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Supporting Information Available: Experimental procedures for the HDS catalyst screen and the syntheses of **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Jandeleit, B.; Turner, H. W.; Uno, T.; Van Beek, J. A. M.; Weinberg, W. H. *Cattech* **1998**, *2*, 101−123.
(2) Jandeleit, B.; Weinberg, W. H. *Chem. Ind. (London)* **1998**, 795−798.
(3) Jandeleit, B.; Schaefer, D. J.; Powers, T. S.; Turner, H. W.; Weinberg, W. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2494−2532.
(4) Senkan, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 312−329.
(5) Thomas, J. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3588−3628.
(6) Weinberg, W. H.; Jandeleit, B.; Self, K.; Turner, H. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 104−110.
(7) Kabe, T.; Ishihara, A.; Qian, W. *Hydrodesulfurization and Hydrodenitrogenation: Chemistry and Engineering*; Wiley-VCH: New York, 2000.
(8) U.S. Environmental Protection Agency. Tier 2/Gasoline Sulfur Final Rulemaking. http://www.epa.gov/otaq/tr2home.htm (accessed Jan 2003).
(9) Hannerup, P. N. *Chem. Ind. Dig.* **1997**, *10*, 112−115.
(10) Shafi, R.; Hutchings, G. J. *Catal. Today* **2000**, *59*, 423−442.
(11) Cooper, A. C.; McAlexander, L. H.; Lee, D.; Torres, M. T.; Crabtree, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 9971−9972.
(12) Shaughnessy, K. H.; Kim, P.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 2123−2132.
(13) Reddington, E.; Sapienza, A.; Gurau, B.; Viswanathan, R.; Sarangapani, S.; Smotkin, E. S.; Mallouk, T. E. *Science* **1998**, *280*, 1735−1737.
(14) Bandarage, U. K.; Simpson, J.; Smith, R. A. J.; Weavers, R. T. *Tetrahedron* **1994**, *50*, 3463−72.
(15) Salem, A. S. H.; Hamid, H. S. *Chem. Eng. Technol.* **1997**, *20*, 342−347.
(16) Takahashi, A.; Yang, F. H.; Yang, R. T. *Ind. Eng. Chem. Res.* **2002**, *41*, 2487−2496.

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