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Hydrodesulfurization with RuS_2 at low hydrogen pressures

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At low hydrogen pressures, is there an inherent limit beyond which additional hydrodesulfurization (HDS) activity may not be achievable within the operating envelope of existing HDS process? In seeking an answer, we offer the following observation: RuS_2 achieves deep HDS of a refractory petroleum distillate at hydrogen pressure as low as 0.79 MPa.

KEY WORDS: deep hydrodesulfurization; RuS_2 catalyst; hydroprocessing at low pressures; HDS of diesel fuels.

1. Introduction

In the face of ever-tightening sulfur level in on-road diesel fuels, sulfur removal from refinery products will become increasingly important in years to come. Currently, diesel fuel's sulfur specification in many countries is 0.05 wt%. In the near future, the specification will go down below 10 wppm or less. Conventional hydrodesulfurization (HDS) catalysts can remove a major portion of the sulfur from diesel fuels, but lack the desired activity for HDS of refractory heterocycles in which the sulfur heteroatom is sterically hindered. This is especially true at low hydrogen pressures (say, 0.79–2.4 MPa). Hydrogen partial pressure is a critical operating variable affecting the cost of sulfur removal. There is every incentive to achieve deep HDS at low hydrogen pressures to minimize capital investment and preserve crude slate flexibility.

It is widely known that over MoS_2-based catalysts, HDS of refractory multi-ring sulfur species is a high hydrogen intensity process in that the principal HDS pathway goes through prehydrogenation of one of the aromatic rings [1–4]. As a result, deep HDS at low hydrogen pressures faces many potentially insurmountable obstacles. First, the hydrodenitrogenation (HDN) rate may be so slow that nitrogen compounds block off virtually all active sites that are otherwise available for HDS [1–6]. Second, the HDS rate of refractory sulfur species may be limited by thermodynamically mandated low hydrogenation rate [3,7]. Third, the catalyst surface may be starved of adsorbed hydrogen. Here, one notes that HDS occurs in the liquid phase owing to capillary condensation even at low pressures. As an example, figure 1 shows the sensitivity of H_2 solubility to hydrogen pressure for a light catalytic cycle oil (LCO). The solubility (mole fraction) at 5.5 and 0.7 MPa are 0.062 and 0.005, respectively. Low solubility also means slow liquid mass transfer because of a weak driving force.

The foregoing considerations may beg the question: At very low hydrogen pressures, is there an inherent limit beyond which additional HDS activity is virtually impossible to achieve without having to use impractically high temperature and/or low space velocity? This is the question to which the present study is addressed. In seeking an answer, we turn to a bulk RuS_2 catalyst whose high volumetric activity has been unmatched by any other transition metal sulfide in previous HDS tests with dibenzothiophene (DBT) at 3.21-MPa hydrogen pressure [8]. In this work, we test the bulk RuS_2 catalyst against a sulfided $CoNiMo/Al_2O_3$-SiO_2 commercial HDS catalyst at 0.79 to 3.21 MPa with an LCO, a most tough-to-desulfurize middle distillate.

2. Prior studies

The extraordinarily high activity of bulk RuS_2 was reported by Pecoraro and Chianelli [8] in their study of the periodic trend of transition metal sulfides (TMS) in HDS of DBT. RuS_2 is at the top of the volcano plot for the second row of TMS, suggesting an electronic effect [9]. Subsequent studies showed that the bulk electronic structure is indeed an important factor controlling the activity of TMS [10,11]. Another important factor is geometric in nature in that RuS_2 has a completely isotropic cubic structure identical to pyrite, which gives rise to a linear correlation between HDS activity and the BET surface area and oxygen chemisorption [9]. This is not the case with MoS_2, which has a highly anisotropic layered structure.

The work of Pecoraro and Chianelli [8] has stimulated considerable interest in RuS_2. Various RuS_2 catalysts, either in bulk or supported form, have been found to be active for HDS, HDN, and hydrogenation [4,12–18]. Tatarchuk and coworkers have addressed many fundamental aspects of bulk and supported RuS_2 catalysts [19–22]. All of these prior studies were done

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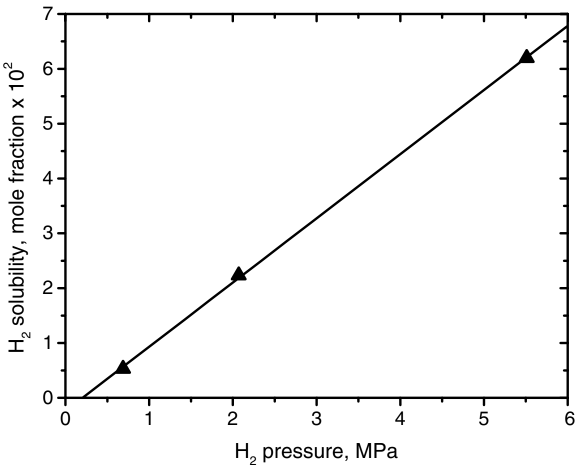

Figure 1. Hydrogen solubility in LCO versus hydrogen pressure at 316 °C.

with model compounds such as thiophene and DBT. A practically important question left unanswered is how RuS_2 stacks up against commercial HDS catalysts in real-feed tests, especially with a *refractory* middle distillate such as LCO at *low* hydrogen pressures.

3. Experimental

3.1. Feedstock and catalysts

Table 1 lists the properties of the LCO feedstock that contains 1.47 wt% total sulfur and 80 wt% aromatics. Here β-DBT represents singly hindered alkyldibenzothiophenes (e.g., 4-methyldibenzothiophene), whereas $\beta\beta$-DBT stands for doubly hindered alkyldibenzothiophenes (e.g., 4,6-dimethyldibenzothiophene). With this tough feed, one must remove some of the sterically hindered DBTs in order to meet the current 0.05 wt% sulfur specification.

Table 1
Feedstock inspection

API	10.6
S, wt%	1.46
N, ppm	554
H, NMR, wt%	8.59
GCD distillation	
1/5	327/451 °F
10/20	467/496 °F
30/40	571/532 °F
50/60	551/575 °F
70/80	601/633 °F
90/95	666/686 °F
99	730 °F
HPLC, LV%	
Saturates	13.0
Total aromatics	87.0
1 Ring	9.3
2 Ring	57.1
3 Ring	20.6
DBT, wt%	21.21
β-DBT	14.60
$\beta\beta$-DBT	4.77
Total DBTs	40.58
DBTs, wt%	0.3097
β-DBTs	0.2131
$\beta\beta$-DBTs	0.0697

The bulk RuS_2 catalyst, with a BET surface area of $60\,m^2/g$, was prepared by J. D. Passaretti by sulfiding $(NH_4)_2RuCl_6$ with pure H_2S at 350 °C for 2 h. The commercial $CoNiMo/Al_2O_3\text{-}SiO_2$ catalyst was sulfided with a 10% H_2S-in-H_2 mixture at 360 °C for 1 h. Both catalysts were crushed and sieved into 20–40 mesh granules.

3.2. Reactor and procedures

The comparative experiments were conducted in two parallel isothermal, concurrent, up-flow, fixed-bed reactors (3/8-inch i.d. 316 stainless steel pipe) in a common sand bath. Each reactor, equipped with a feed burette, pump, gas–liquid separator, and product collector, contains 10 cc catalyst in the central zone and inert diluents in the fore and aft zones. Table 2 lists the four sets of conditions used in this study.

After purging with nitrogen, the liquid product was analyzed for total sulfur by X-ray fluorescence using external standards. This was done with a Princeton Gamma-Tech Model 100 Chemical Analyzer, which contains an ^{55}Fe radioactive source. The total nitrogen was analyzed by combustion and chemiluminescence using the Antek analyzer. The product gases were vented through a caustic scrubber followed by a wet test meter.

4. Results and discussion

Figures 2 and 3 show the extents of HDS and HDN versus time on stream at conditions A to D. After the start-up, both catalysts quickly lined out their HDS activities. But it took a long time for RuS_2 to equilibrate its HDN activity. The volumetric HDS and HDN activities of RuS_2 are both much higher than those of the commercial catalyst. Specifically, RuS_2 showed roughly a five-fold HDS and a two-fold HDN advantages over sulfided $CoNiMo/Al_2O_3\text{-}SiO_2$ based on

Table 2
Reaction conditions A to B

Condition	H_2 (MPa)	Temp (°C)	LHSV[a]	scf/bbl[b]
A	3.21	325	3	3000
B	2.38	343	1	1000
C	1.48	343	1	1000
D	0.79	343	1	1000

[a] Liquid hourly space velocity.
[b] Standard ft^3 H_2/barrel of liquid feed.

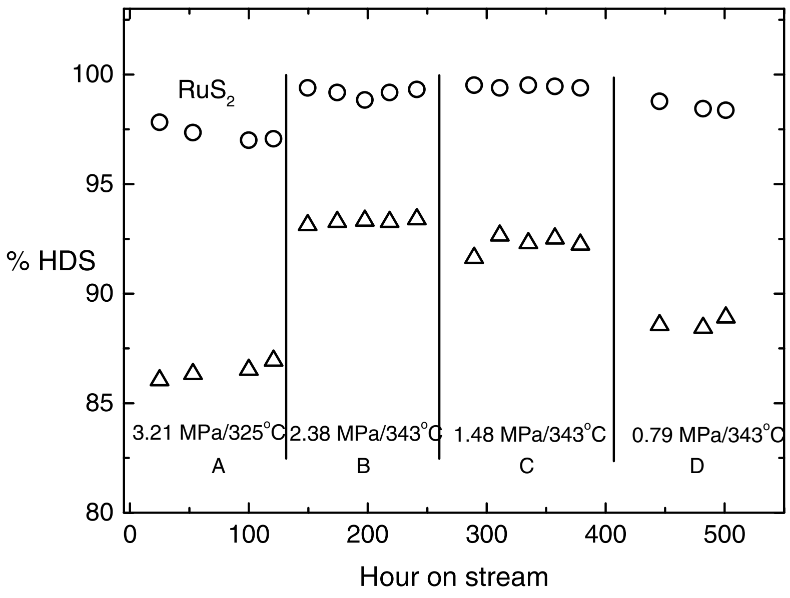

Figure 2. Percent HDS versus on-stream hour at conditions A to D. Open circles: RuS_2; triangles: sulfided $CoNiMo/Al_2O_3$-SiO_2.

second-order HDS kinetics and first-order HDN kinetics at condition A. Hence, the main advantage of RuS_2 lies in HDS. This is also borne out by the data obtained at other conditions, as shown in figures 2 and 3.

Note that in going from condition A to condition B, the hydrogen pressure is lowered while the temperature is increased. Here, the HDN activity of the commercial catalyst provides a tie-point in that the two conditions give essentially the same HDN level (≈ 40%). The percent HDN with RuS_2 at condition B is lower than that at condition A. In contrast, HDS rates on RuS_2 and sulfided $CoNiMo/Al_2O_3$-SiO_2 are both noticeably higher at condition B than at condition A. These results indicate that with either catalyst HDS is more sensitive to temperature than HDN. Also HDN, relative to HDS, is more responsive to hydrogen pressure than to temperature. It should be noted that here the extent of HDS largely reflects the sulfur removal from non-refractory sulfur compounds (e.g., DBT) that constitute

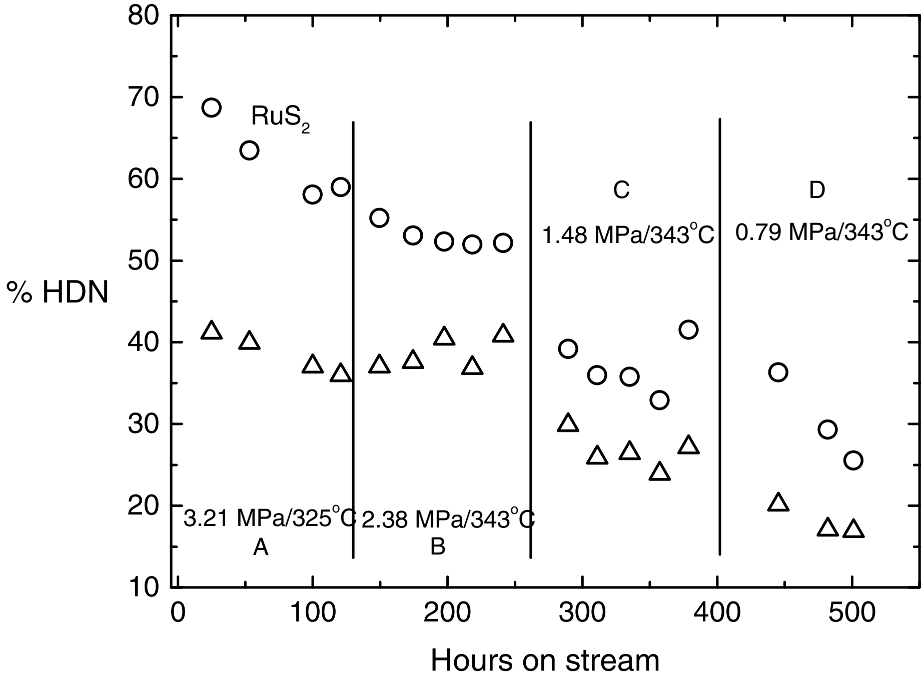

Figure 3. Percent HDN versus on-stream hour at conditions A to D. Open circles: RuS_2; triangles: sulfided $CoNiMo/Al_2O_3$-SiO_2.

the majority of the indigenous sulfur species. HDS of such sulfur species predominantly proceeds through the hydrogenolysis pathway (direct C–S bond scission), which may have a high activation energy and hence a stronger temperature response. Another factor is that the high temperature at condition B may lessen competitive adsorption of nitrogen compounds on catalytically active sites, thus enhancing the HDS rate. It is reasonable to expect that nitrogen compounds can adsorb on sites where HDS of nonrefractory sulfur compounds take place—even though they may or may not denitrogenate there.

As figure 2 shows, the RuS_2 catalyst desulfurizes nearly all sulfur species at hydrogen pressures between 1.48 and 2.38 MPa, indicating that the catalyst in the reactor downstream zone may not be fully utilized. The hydrogen pressure was then further lowered to 0.79 MPa. Defying the odds, RuS_2 can still give an HDS as high as 98.4%, corresponding to a product sulfur of 235 ppm. At this level of HDS, the catalyst clearly attacks sterically hindered DBTs. For perspective, the commercial catalyst reduces sulfur down to only 1000 ppm (93.2% HDS) at a much higher hydrogen pressure of 2.38 MPa.

Figure 4 summarizes the effect of pressure on HDS. As can be seen, even at 2.38 MPa the commercial catalyst does not produce a liquid product meeting the 0.05% sulfur specification currently adopted by many countries. If we assume that HDS of $\beta\beta$-DBT does not occur until almost all of the reactive sulfur compounds and β-DBT are desulfurized, then the onset of HDS of $\beta\beta$-DBTs can be indicated in figure 4 by the horizontal dashed line, below which no sulfur removal from $\beta\beta$-DBTs occurs (figure 4). One thus sees that a striking difference between the two catalysts is that RuS_2 can readily desulfurize $\beta\beta$-DBTs at 0.79 MPa, while this is not the case with the commercial catalyst even at a higher hydrogen pressure of 2.38 MPa. Moreover, RuS_2 does so in an environment presumably quite susceptible to poisoning by nitrogen species because of RuS_2's low HDN activity at 0.79 MPa. It seems, then, that the active sites for HDS of $\beta\beta$-DBTs on RuS_2 may be less vulnerable to nitrogen poisoning than those on conventional MoS_2-based catalysts. A final point of note is that it is not possible to quantify the activity of RuS_2 because it gives nearly 100% HDS at 1.58 and 2.38 MPa. What we do know, however, is that HDS of LCO is a high-order reaction [23]. As such, even a small difference in percent HDS at high HDS levels means a big difference in activity. Also, the intrinsic activity of RuS_2 might be higher than that indicated by the data in figure 4 because a high-order reaction at high conversions is more susceptible to axial dispersion in small reactors.

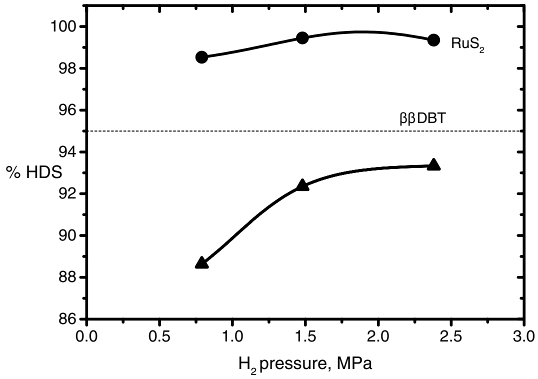

Figure 4. Percent HDS versus hydrogen pressure at 343 °C. The horizontal dashed line indicates the onset of removing sulfur from $\beta\beta$-DBTs.

5. Concluding remarks

RuS_2 is a far more active HDS catalyst than a commercial supported catalyst on a volumetric basis. It reduces the sulfur level of a very refractory middle distillate from 1.46 wt% to 235 ppm at a relatively fast rate at a hydrogen pressure as low as 0.79 MPa. This result suggests that no inherent kinetic limitation exits on HDS at low hydrogen pressures. This statement, however, must be tempered by the fact that the available data do not cover ultra deep HDS regime, say, less than 30 wppm product sulfur.

It is unclear why RuS_2 is so active for removing sterically hindered sulfur compounds under "harsh" conditions. We speculate that steric hindrance may not be as important a factor for RuS_2 as for conventional MoS_2-based catalysts. It is also possible that RuS_2 is less sensitive to organonitrogen poisoning and/or more effective in activating hydrogen.

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