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# Influence of ammonia on thiophene HDS at high pressures over noble metal catalysts for deep HDS applications

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## Abstract

The thiophene hydrodesulfurization (HDS) activity of Pt/ASA, Pt/$SiO_2$, Ir/ASA and Ir/$SiO_2$ catalysts at thiophene concentrations of 300 ppm has been studied at 573 K and 20 bar. Pt/ASA showed the highest HDS activity. Nitrogen tolerance was investigated by co-feeding ammonia in gas phase concentrations from 10 to 1000 ppm. The amorphous silica alumina (ASA) supported catalysts were similarly strongly inhibited by the presence of ammonia, with even 10 ppm of ammonia causing a significant drop in activity, despite widely different dispersions. The $SiO_2$ supported catalysts were less severely affected by the presence of ammonia.

*Keywords:* Deep HDS; Nitrogen poisoning of HDS; Noble metals in deep HDS

## 1. Introduction

Legislation on diesel fuel quality has become increasingly stringent because of environmental concerns, and can be expected to be more so in the future [1]. To achieve deeper levels of hydrodesulfurization (HDS) than the currently permitted S level of 500 ppm and lower aromatic content requires improved catalysts and processes avoiding higher temperatures and pressures [1,2]. In an earlier study of refractory sulfur compounds [3], it was shown that Pt supported on an amorphous silica alumina (ASA) was highly active for deep HDS of 4-methyl,6-ethyl DBT; where it was considered that the sulfur tolerance was associated with the acidic nature of the carrier [4]. However, the performance was not maintained for processing of real desulfurized gas oil due to the presence of nitrogen compounds [3]. Clearly, inhibition of HDS and aromatic hydrogenation by N-compounds [3–9] is an important factor in the development of new very deep HDS processes and the exploitation of precious metal catalysts. The nitrogen tolerance of precious metal catalysts at deep HDS conditions has not been extensively studied.

In this work the HDS activities of the precious metals Pt and Ir on two very different supports, amorphous silica alumina (ASA) and amorphous silica, have been investigated in the context of their relative tolerance to ammonia at deep HDS sulfur levels. Thiophene HDS at 573 K and 20 bar total pressure was chosen as the test reaction with a thiophene concentration of 300 ppm – an intermediate deep HDS sulfur level between current and future limits. The dependence of the nitrogen tolerance of these catalysts on the active metal and the nature of the

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support was investigated by co-feeding ammonia in concentrations of up to 1000 ppm.

## 2. Experimental

### 2.1. Catalysts and characterization

The Pt/ASA and Ir/ASA catalysts and ASA carrier were supplied by Shell Research and Technology center. Metal loadings were 0.8 wt% Pt and 1.0 wt% Ir determined by ICP. The ASA carrier has a Si/Al ratio of 1.6:1 and a BET surface area of 400 $m^2/g$. The silica supported catalysts were prepared by impregnation of an amorphous silica, EP10 supplied by Crosfield Catalysts (surface area of 325 $m^2/g$), with aqueous solutions of the corresponding chloro-acids. Metal loadings after calcination in air were 5.0 wt% $Pt/SiO_2$ and 4.6 wt% $Ir/SiO_2$, determined by neutron activation analysis. XPS analysis did not reveal any chlorine retention. TPR experiments showed that the catalysts were all fully reduced under the reaction conditions. The catalysts were crushed and sieved to give catalyst particles of diameter 125–250 µm. Dispersion was measured by $H_2$ chemisorption.

### 2.2. Reactor system and HDS experimental procedure

The HDS experiments were performed at 20 bar and 573 K in a continuous stainless steel fixed-bed microreactor using a SiC diluent to catalyst ratio of 5/1. Reduction was carried out in situ at 573 K and atmospheric pressure in a flow of 246 ml/min (STP) of $H_2$ for 1 h. The liquid feed of 1 wt% thiophene in heptane and covered with an inert nitrogen blanket was combined with a hydrogen flow using a HPLC pump, evaporator and mixer to obtain a thiophene concentration in hydrogen of 300 ppm. Adjustment of the liquid flow rate allowed the thiophene concentration to be varied. Ammonia was added to the hydrogen feed from premixed cylinders of $NH_3$ in $H_2$ containing 100 and 1000 ppm, respectively, using a two channel mass flow controller system. After the initial steady-state was achieved at $NH_3$ free conditions, the $H_2$/thiophene feed gas was switched to a $H_2/NH_3$/thiophene feed and a new steady-state was achieved. Experiments with increasing $NH_3$ concentrations were carried out sequentially.

## 3. Results and discussion

### 3.1. Thiophene HDS

The thiophene HDS activities of the catalysts at steady-state in the absence of ammonia are given in Fig. 1. Typically, steady-state was achieved after 6 h and data collected for a further 2 h. The main desulfurized product observed from all the catalysts was *n*-butane with only small amounts of butene present. Selectivity to tetrahydrothiophene was significant, 10–30%, at the experimental conditions and in general was found to increase with decreasing conversion, as would be expected from the sequential hydrogenation of thiophene to tetrahydrothiophene followed by hydrogenolysis to $C_4$'s. No significant hydrocracking was observed, although trace amounts of $C_3$, $C_5$ and $C_6$ hydrocarbons were detected. The higher activity of the ASA supported catalysts compared to the silica catalysts, whether on a per unit mass or per mmol of adsorbed $H_2$, is consistent with the known greater sulfur tolerance of precious metals on acidic supports [4]. Measurements on the ASA supported catalysts with higher thiophene concentrations confirmed that thiophene HDS activity decreased with increasing concentration of sulfur. The Pt/ASA catalyst showed the highest activity on a per gram basis. However, allowing for the relative dispersion, Table 1, Pt and Ir catalysts showed comparable activity expressed per mmol of adsorbed $H_2$ irrespective of the support. This

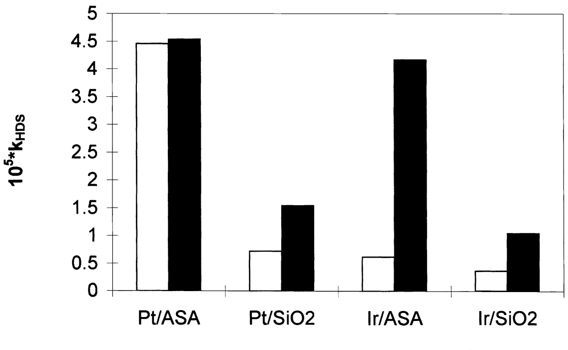

Fig. 1. Catalyst HDS activities □ ($mol_{thiophene}/s^* g_{metal}$); ■ ($mol_{thiophene}/s^*$mmol $H_2$ adsorbed).

Table 1
Catalyst dispersion

| Catalyst | Dispersion (%) |
|---|---|
| Pt/ASA | 38.4 |
| Pt/$SiO_2$ | 18.3 |
| Ir/ASA | 5.7 |
| Ir/$SiO_2$ | 13.4 |

contrasts to previously reported low activity of Ir/ASA [10].

### 3.2. Ammonia tolerance

The inhibiting effect of $NH_3$ on hydrotreating catalysts is well known [3,6–8]. However, for precious metal catalysts under HDS conditions the effect has rarely been quantitatively studied [3,4]. The influence of $NH_3$ on the steady-state thiophene HDS activities of the Pt and Ir catalysts is shown in Fig. 2, expressed as $k_{HDS}/k_{HDS_{initial}}$. Steady-state was achieved for each concentration after 6–8 h on stream. Experiments with increasing $NH_3$ concentrations were carried out sequentially with the same catalyst. As a check on the reproducibility of the approach, an additional measurement was carried out going directly from $NH_3$ free conditions to 1000 ppm. The same decrease in activity was observed at 1000 ppm $NH_3$ compared with the sequential method.

$NH_3$ had a similar drastic negative effect on the HDS activity of both the Pt/ASA and Ir/ASA catalysts, despite the large difference in dispersion. Even 10 ppm of $NH_3$ resulted in a significant loss in activity. The activity further decreased with increasing $NH_3$ partial pressure, with the final activity at 1000 ppm $NH_3$ being approximately half of the original no $NH_3$ free value. The effect can be qualitatively understood in terms of a Langmuir–Hinshelwood–Hougen–Watson (LHHW) model in which $NH_3$ inhibits the rate of HDS by competitive adsorption. Such a model would predict a lower sensitivity to $NH_3$ at higher sulfur concentration. Indeed, this was confirmed for the Pt/ASA catalyst in a preliminary experiment [11] carried out with 10 times the thiophene concentration. The relative effect of ammonia was less severe than that at the lower thiophene concentration; $k/k_{initial}$ was 0.7 as opposed to 0.5, although the total HDS activity was lower at the higher S level. These results contrast with a study of the effect of $NH_3$ on toluene hydrogenation at 60 bar over Pt/alumina by Mignar et al. [9], where at extremely low concentrations of $NH_3$ (<50 ppm) no significant inhibiting effect was observed, but at higher concentrations the hydrogenation rate decreased almost to zero.

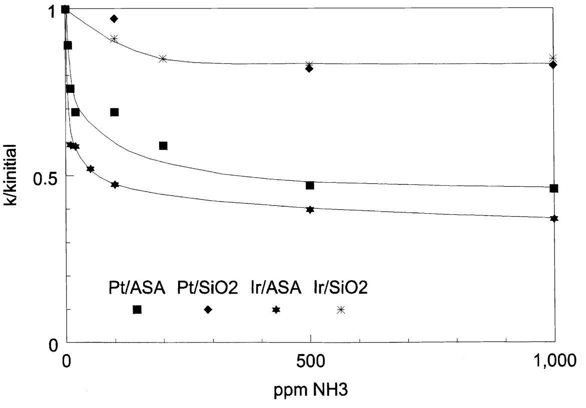

Fig. 2. Relative effect of $NH_3$ on catalyst HDS activities.

The Ir and Pt silica based catalysts both showed a small decrease in HDS activity, even when high levels of ammonia were present. The dispersions were also similar. However, comparison of the HDS activities and $NH_3$ tolerance behavior with the ASA supported catalysts, and taking into account the widely differing dispersions, the results are consistent with the view that acidic carriers impart sulfur tolerance, but increase sensitivity to nitrogen bases, while the converse is also true [4].

In principle the data shown in Fig. 2 could be used to determine the form of the rate equations by fitting various LHHW models. One of the initial interests of the study was to investigate the form and transferability of rate equations between various precious metals and different supports. From the present experimental results, it is only for the ASA catalysts that this is potentially possible. If a single site model is assumed, then the data for the these catalysts is consistent with a high negative order with respect to ammonia (possibly as high as −5). A high negative order could be interpreted in terms of a hydrogenation reaction with dissociated hydrogen as the rate determining step.

For the ASA catalysts the rate of HDS did not drop to a very low relative value at 1000 ppm $NH_3$, as would be expected from simple LHHW kinetics and is observed over conventional hydrotreating catalysts [4,12]. Rather, it leveled out to approximately half the original value. One possibility is that there is a change in desulfurization mechanism when high $NH_3$ concentrations are present, e.g. a shift in the rate determining step [13] and form of the rate equation [9]. However, butene selectivities did not change appreciably with increasing amounts of $NH_3$, as would be expected if there were a change in reaction pathway. A more likely explanation is associated with the adsorption characteristics of $NH_3$ on platinum surfaces. Studies of $NH_3$ adsorption on Pt single crystal surfaces at low pressures [14–16] reveal two types of adsorbed $NH_3$ – a low coverage state of $\theta<0.4$ which desorbs over a wide range of temperatures (120–500 K) indicating a strongly coverage dependent heat of adsorption, and a high coverage state of $\theta>0.4$, which desorbs sharply at low temperature (120 K). No evidence was found for dissociative adsorption of $NH_3$. At saturation $\theta\approx1$, $\Delta H_{\mathrm{ads}}$ is reported to be as low as 40 kJ/mol. It seems likely that these factors limit the achievable surface $NH_3$ coverage at the temperature, hydrogen and thiophene pressures used in the present study.

The inhibition effect of $NH_3$ was not fully reversible for all catalysts, as reported in other studies [9]. The effect was reversible for Pt/ASA, but only partially reversible for Ir/ASA, which showed the highest butene selectivity. Pt/$SiO_2$ and Ir/$SiO_2$ showed evidence of irreversibility, but the inhibition effects were in any case small. Ammonia may play a role in increasing coke formation and it is possible that this may contribute to the irreversibility. Analysis of spent catalyst samples was not possible because the samples were diluted with SiC.

## 4. Conclusion

The acidity of the carrier appears to be a key factor with regard to the $NH_3$ tolerance of the deep HDS activity of the precious metal catalysts. ASA supported catalysts were severely inhibited by the presence of even small amounts of $NH_3$, but for $SiO_2$ supported catalysts the effect was less severe. It would seem [4] that by increasing the sulfur tolerance of precious metal catalysts using acidic carriers, the nitrogen tolerance is simultaneously decreased.

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