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Catalytic hydrotreating of heavy gasoil FCC feed over a NiMo/γ-Al_2O_3-TiO_2 catalyst: Effect of hydrogen sulfide on the activity

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Abstract

An experimental study was conducted in a pilot plant fixed-bed reactor in order to evaluate the effect of hydrogen sulfide on hydrotreating activity of an industrial heavy gasoil Fluid Catalytic Cracking (FCC) feed recovered from a Mexican refinery. Hydrotreating reactions were carried out at three temperatures (603, 638 and 673 K), 11.76 MPa of pressure and LHSV of 6 h^{-1}. Studies were done varying hydrogen sulfide concentration 0, 100, 450 and 750 vol ppm (0, 3100, 12,960 and 23,210 Pa, respectively) at the same operating conditions over a commercial NiMo/γ-Al_2O_3-TiO_2 catalyst. Experimental results showed different behavior for these reactions. An inhibiting effect on hydrodesulfurization (HDS), hydrodearomatization (HDA) and hydrodenitrogenation (HDN) was observed, whereas the hydrodemetallization (HDM) reaction showed an increase in the activity. Apparent activation energies were also determined for each reaction.

Keywords: H_2S effect; Hydrodesulfurization; Hydrodenitrogenation; Heavy gasoil hydrotreatment

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1. Introduction

The stringent environmental requirements for emissions have led to quality improvements in fuel products in terms of reduction in aromatics and heteroatoms mainly sulfur [1]. Since the FCC gasoline is the main contributor of sulfur to the gasoline pool, several approaches have been applied to meet sulfur levels in fuels. The pretreatment of FCC feed has allowed refiners to fulfill the new fuel specifications with concomitant improvement of the Fluid Catalytic Cracking Unit (FCCU) operation [2–5]. The hydrotreating process can be designed to perform either in two reaction stages or in one reactor with two catalytic beds [6–8] and the selection of catalysts depends on the product objectives. The CoMo catalysts are preferred when the HDS is the main aim whereas NiMo catalysts are the preferred option when aromatics saturation, hydrodenitrogenation and metal removal are the main objective. It is known that the hydrodesulfurization reaction affords hydrogen sulfide, and tends to inhibit the hydrotreating reactions. This fact has attracted great interest and different studies about the effect of H_2S on the HDS reaction of model compounds [9–11] as well as of real feedstocks have been undertaken [12,13]. The effect of hydrogen sulfide on the HDN reaction has also been studied using model compounds such as pyridine, indole, aniline derivatives and tetrahydroquinone [14–20] and also using gasoil [13,21]. Additionally, several works of HDM of vacuum residue and model compounds such as porphyrins have also been published [22–28], however, few of them deal with the effect of H_2S [29,30]. It is important to mention that an increase in the hydroprocessing of heavy crudes such as Maya is envisaged in Mexican Refineries in the near future, these new feedstocks will contain higher amounts of aromatics, heteroatoms and metals. Therefore, it is essential to carry out studies with heavy gasoils FCC feed in order to gain information about how these new feedstocks will affect the reactions involved in the hydrotreating process. In connection with this line of research, we recently reported a

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study of hydrotreating activity of heavy gasoil FCC feed operating at high LHSV [31,32]. In continuation with our interest in the hydroprocessing of heavy gasoils, we describe herein the effect of hydrogen sulfide on the HDS, HDA, HDN and HDM of a real feedstock recovered from a Mexican refinery, the study was carried out using a commercial NiMo/γ-Al_2O_3-TiO_2 catalyst varying hydrogen sulfide concentration and operating at high LHSV.

2. Experimental

2.1. Hydrotreating catalyst and presulfiding conditions

The hydrotreating catalyst used in the present study was a NiMo/γ-Al_2O_3-TiO_2 commercially available sample and its properties are summarized in Table 1. The hydrotreating tests were carried out under steady-state operation in a fixed bed pilot plant operating in down-flow mode. The pilot reactor is made of a stainless steel tube; the length and internal diameter of the reactor are 143 and 2.54 cm, respectively. The reactor is divided into three sections. The first section was packed with helly-pack and was used to heat up the mixture to the desired reaction temperature. The second section contained the catalyst and the final section was also packed with helly-pack. The properties of the gas oil used in the evaluations are shown in Table 2. API gravity, sulfur, metals, aromatics and total nitrogen content in the feedstock were determined by the D-287, D-4294, D-5708, D-5186 and D-4629 ASTM methods. The catalyst was activated in situ by sulfiding with desulfurized naphtha contaminated with 0.6 wt% CS_2 for 12 h at 5.49 MPa, temperature of 503 K and LHSV of 2.5 h^{-1}.

2.2. Hydrotreating Tests

After completion of the catalyst sulfidation procedure, the hydrocarbon stream was switched to the evaluation feedstock. The reactor temperature was raised from that of activation (503 K) to 603 K and a stabilization period until no appreciable variations in temperature (2 h) was allowed. Two experiments were performed for each condition. All experiments were carried out at a constant reaction pressure of 11.764 MPa, H_2/Oil ratio of 322 (m^3 std)/m^3 and LHSV of 6 h^{-1}, H_2S concentration (0, 100, 450 and 750 vol ppm), four different samples of fresh catalysts were used for each experiment. Reaction temperature was studied at 603, 638 and 673 K. The volatile components of the samples obtained from each temperature were stripped off by distillation at 473 K (pressure of 101.32 kPa). The reactor temperature was maintained at the desired level by using a three-zone electric furnace, which provided an isothermal temperature along the active reactor section. Fig. 1 shows three typical temperature profiles obtained from the reaction temperatures, the highest deviation from the desired temperature value was found to be about 1 K. During the evaluations no appreciable deactivation was observed which was monitored by check-back experiments to the initial test temperature.

Table 1
Physical and chemical properties of the commercial catalyst

Mo (wt%)	9.52
Ni (wt%)	2.42
Ti (wt%)	5.69
Metal loading (wt%)	11.94
Atomic ratio (Ni/Ni + Mo)	0.29
Density (g cm^{-3})	0.82
Surface area (m^2 g^{-1})	182
Total pore volume (cm^3 g^{-1} N_2)	0.43
Pore average diameter (Å) (N_2)	95

Table 2
Physical and chemical properties of heavy gasoil FCC feed

°API	22.9
Specific gravity (oil$_{20\,^\circ C}$/water$_{4\,^\circ C}$)	0.912
Sulfur (wt%)	2.84
Metals (Ni+V) (ppm)	1.1
Aromatics (wt%)	51.6
Mono-aromatics (wt%)	29.1
Di-aromatics (wt%)	15.2
Poly-aromatics (wt%)	7.3
Total nitrogen (N) (ppm)	1353

The apparent rate constants for HDS were determined by using Eq. (1) with a pseudo 1.5 order (referred to S concentration).

$$k = \left[\frac{1}{S_P^{0.5}} - \frac{1}{S_F^{0.5}}\right]\frac{\text{LHSV}}{(n-1)} \qquad (1)$$

where k: pseudo 1.5 order HDS kinetic constant ($ppm^{-0.5}h^{-1}$); S_P: sulfur in product (wt ppm); S_F: sulfur in feedstock (wt ppm); LHSV: liquid hourly space velocity (h^{-1}).

Whereas for HDM, HDA and HDN reactions a pseudo first order model was assumed. Thus, the corresponding apparent rate constants were calculated using Eq. (2).

$$k_{HDX} = \ln\left(\frac{X_F}{X_P}\right)\text{LHSV} \qquad (2)$$

where k_{HDX}: pseudo first order HDA, HDN or HDM kinetic constant (h^{-1}); X_F: aromatics (wt%), total nitrogen or metals in the feedstock (wt ppm); X_P: aromatics (wt%), total nitrogen or metals in the product (wt ppm).

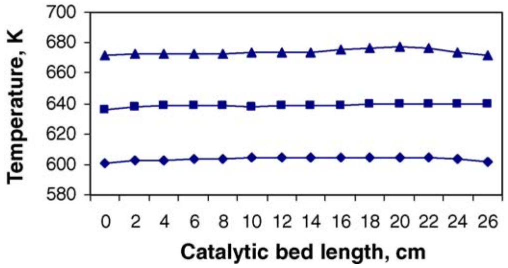

Fig. 1. Temperature profiles in the catalytic bed.

3. Results and discussion

The effect of the hydrogen sulfide concentration on the hydrotreating activity was investigated from 0 to 750 vol ppm and the results of the four different reactions are shown in Figs. 2–5. The corresponding HDS, HDA, HDN and HDM apparent activation energies (E_a) were calculated from the slopes of straight lines and are summarized in Table 3, which shows that calculated values agreed with those published in the literature for each reaction [33,34]. The apparent activation energies are also shown in Table 3 which are approximately similar and significant changes with the increase of H_2S concentration are not observed.

The removal of sulfur as a function of the hydrogen sulfide concentrations is depicted in Fig. 2 which shows the results of the HDS activity in terms of apparent rate constant k_{HDS}. It is observed that the activity decreases as soon as H_2S is added to the feed, however, the HDS activity seems to stabilize at high concentrations of hydrogen sulfide. This result shows that H_2S effect on the hydrotreating of this gasoil is basically the same to those reported for model compounds and real feedstocks [9,10,12,13]. It is worth mentioning that there is no further significant effect when H_2S concentration increases from 450 ppm (12,960 Pa) to 750 ppm (23,210 Pa), which agreed with a previous report that showed that the inhibitory effect of hydrogen sulfide on the HDS reaction of model compounds is negligible over 250 Pa of H_2S partial pressure [10]. The stable activity plateau of HDS reaction with increasing H_2S in the feed is suggested to be evidence of reaching a saturation level of the surface active sites that could be modified by H_2S.

Another important reaction involved in the pretreatment of FCC feed is the hydrogenation of aromatic compounds. It is known that aromatic compounds are not easily cracked in the FCC Unit and the limited amount of cracking achieved affords a large amount of coke, thus it is also convenient to consider the H_2S effect on the hydrogenation reaction. The inhibiting effect of H_2S on the hydrogenation of model compounds such as biphenyl, propylbenzene and naphthalene has been summarized by Girgis and Gates [35]. Fig. 3 depicts the activity of the hydrodearomatization reaction for the three different H_2S concentrations, which shows that the H_2S inhibits the HDA in the same way to that observed in the HDS reaction. However, it should be noted that the effect does not increase with temperature and it becomes stable. The results obtained from this study showed that the behavior is quite similar to that found in model compounds. Additionally, appreciable differences in the liquid density product were not observed despite the fact that the hydrogenation of aromatic compounds decreases when H_2S is added.

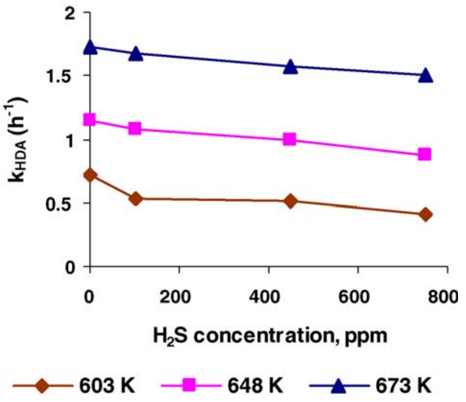

Fig. 3. HDA activity as H_2S concentration function.

Since in practice the hydrotreating removes simultaneously sulfur and nitrogen the effect of H_2S on hydrodenitrogenation is also important. Taking this into account, several studies concerning reactivity and mechanisms of HDN have been undertaken [17,20,36], some of them report that hydrogen sulfide inhibits the hydrogenation of heteroaromatic compounds but favors the hydrogenolysis of C–N bonds. Our results of the effect of H_2S on HDN activity seem to support the former suggestion, which are depicted in the Fig. 4. We can see that the activity decreases as the H_2S concentration increases. Nevertheless, it should be noted that the most significant decline is observed at 100 vol ppm of H_2S as shown in the HDS reaction. Eventually, the decrease becomes constant to higher concentration which is in agreement with a study reported by Ancheyta-Juárez [13].

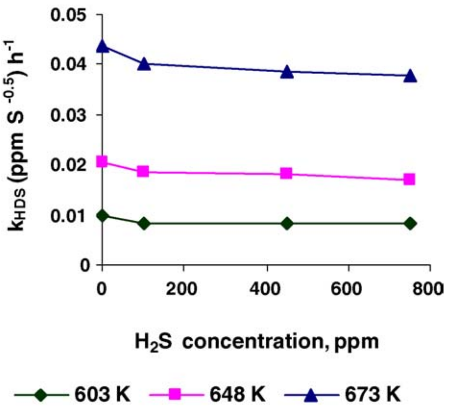

Fig. 2. HDS activity as H_2S concentration function.

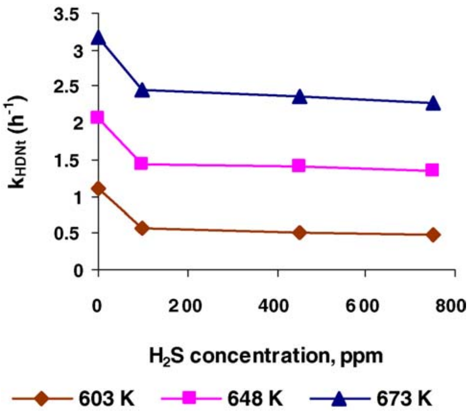

Fig. 4. HDN activity as H_2S concentration function.

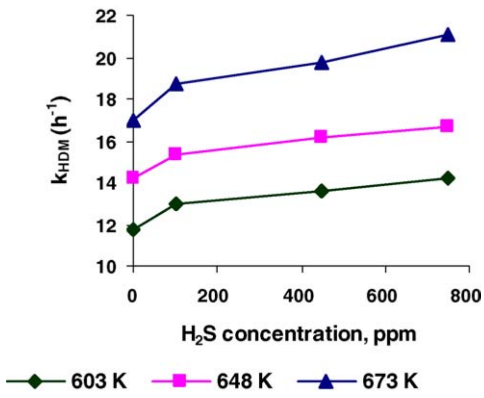

Fig. 5. HDM activity as H_2S concentration function.

Regarding this, it is well known that in the hydrodenitrogenation of aromatic model compounds the presence of H_2S promotes hydrogenolysis of C–N bonds but inhibits the hydrogenation. The augment of hydrogenolysis is associated with the formation of new sites as a result of the adsorption and dissociation of H_2S molecules which convert sulfur vacancies into Brönsted acid centers, however, the process is reversible if H_2S is removed from the system [37]. It is also reported that the hydrogenolysis is more selective towards C(sp^3)–N bond cleavage than C(sp^2)–N bond [17], which means that removal of nitrogen from aliphatic amines is facilitated by the presence of H_2S whereas the hydrodenitrogenation of aromatic rings is inhibited. The results of our study showed that the HDN reaction is inhibited by hydrogen sulfide which can be attributed to the feedstock which contains significant amounts of polycyclic and heterocyclic aromatic nitrogen species as shown by Laredo et al. [38]. They reported a characterization study of different Mexican gasoils showing the presence of alkyl substituted carbazol type compounds. They also demonstrated that the content of such species increases along with the boiling point of the evaluated gasoils. It is worth noting that these compounds possess C(sp^2)–N bonds, which are the most difficult to break.

Results of HDM activity are depicted in Fig. 5. In contrast with the observed in the HDS reaction, the HDM displays an increase in the activity when the H_2S is added. The temperature influences the behavior in a different way compared to that of the HDS reaction. Fig. 5 shows that as the H_2S partial pressure increases the HDM activity also increases, which is in accordance with earlier findings reported by Bonné et al. [30]. They described that H_2S favors the HDM in absence of a catalyst, which is attributed to the formation of covalent bonds between sulfur and the metal as a result of the high affinity of sulfur towards these metals. Eventually, the H_2S promotes the destabilization of the aromatic porphyrin ring facilitating the hydrogenation which leads to the ring fragmentation [28]. The activation energy values are summarized in Table 3, they seem to be reasonable since it is reported that HDM shows substantial pore diffusion limitation in real feedstock due to the large metal-containing molecules [26].

Table 3
Apparent activation energies (kJ/g mol) measured for HDT reactions of the heavy gasoil at different H_2S concentrations, 117.64 MPa, H_2/hydrocarbons ratio 322 (m^3 std)/m^3 and LHSV = 6 h^{-1}

H_2S concentration (ppm)	HDS	HDA	HDN	HDM
0	71.1	30.8	51.4	17.7
100	75.4	39.1	69.9	17.4
450	74.0	37.2	74.2	18.0
750	73.0	40.7	76.0	19.1

4. Conclusions

The H_2S effect on the hydrotreating of heavy gasoil over a commercial NiMo/γ-Al_2O_3-TiO_2 catalyst has been investigated. The HDS activity decreased as the H_2S concentration increased, however, changes at high concentration were negligible, and in addition, at high temperature the effect decreased as reported in previous studies. It was also found that HDA is inhibited by the presence of H_2S similar to the HDS reaction, which is in accordance with that observed in model compounds; significant variations in the liquid density product were not observed. The hydrodenitrogenation reaction showed an inhibitory effect which contrasts with the studies that have been reported for model compounds, however, it agrees with those of real feedstocks. This fact can be caused by the presence of carbazol type structures which are known to be more refractory towards hydrogenolysis. Additionally, the HDM was found to be favored by the presence of H_2S in which was observed that the HDM increases along with the H_2S concentration.

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