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Ni//Mo synergism via hydrogen spillover, in pyridine hydrodenitrogenation

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ABSTRACT

The pyridine hydrodenitrogenation (HDN) over physically separated stacked Ni//Mo beds was investigated using a continuous-flow high pressure (3 MPa) stainless steel microreactor. Results prove the existence of synergism between physically separated beds of Ni-/γ-Al_2O_3 and Mo/γ-Al_2O_3 catalysts for the pyridine hydrodenitrogenation reaction. This synergism is explained by the formation of hydrogen spillover. Product analysis of the pyridine hydrodenitrogenation over Ni//Mo stacked beds suggested that the hydrogen spillover modified the active sites of the MoS_2 by increasing the hydrogenation sites.

1. Introduction

The catalysts most frequently used in the industrial hydrotreating (HYD) processes generally consist of a binary combination of Mo(or W) and Co(or Ni) sulfides supported on γ-Al_2O_3 [1,2]. The evolution of the different structural models proposed to explain the synergy in hydrodesulfurisation (HDS) catalysts has been summarized in many reviews, e.g. [1–6]. Among the numerous structural models proposed, the two models with major acceptance are the Co(Ni)–Mo–S model of H. Topsøe et. al. [7,8] and the contact synergy/remote control (RC) model developed by B. Delmon and co-workers [9,10]. In this model the synergism is related to a hydrogen spillover species (Hso), which migrates from a donor phase (D = Co_9S_8 or NiS) to an acceptor phase (A = MoS_2 or WS_2) which hereby is activated.

The Co(Ni)–Mo–S model claims that the synergetic effect is due to the formation of the Co(Ni)–Mo–S structure, which consists of small MoS_2-like domains with the promoter atoms (Co and Ni) located at the edges of the MoS_2 layers [7,8]. As the intrinsic activity of this structure depends strongly on the catalyst preparation and activation procedure, two types of Co(Ni)–Mo–S structures, Types I and II, having different intrinsic activity, were proposed [11]. The Type I is formed after low-temperature sulfidation and is characterised by incomplete sulfidation and a lower hydrodesulfurisation (HDS) activity than Type II, which is formed after high-temperature sulfidation and fully sulfided.

Direct, unambiguous evidence for the existence for the RC mechanism was dificult to achieve, since formation of small amounts of the Co(Ni)–Mo–S phase over a catalyst containing Co and Mo can never be totally excluded. Recent studies in our laboratories using a reactor system of physically separated, layered catalyst beds [12–18] have provided further evidence for the RC model in HDS. It was found that the activity of two stacked single beds of monometallic supported Co(or Ni) sulfide (first-layer bed) and Mo sulfide catalysts (second-layer bed) separated by a 5 mm layer of γ-Al_2O_3 or SiO_2 for the HDS reaction with gas-oil was higher than the sum of that observed for the corresponding single-bed monometallic catalysts [12]. This synergistic effect was found to be strongly dependent on the reaction temperature [12–16], the separator's nature [13] and the distance between the separate monometallic catalyst beds [14]. More recently, we detected synergisms in the HDS reaction with gas-oil for Mn//Mo Fe//Mo, Co//Mo, Ni//Mo Cu//Mo and Zn//Mo stacked beds [15]. Also, the positive influence of phosphorous in the classic Co–Mo/γ-Al_2O_3 catalyst was explained by an increase of the Hso mobility between the donor, D (Co_9S_8), and the acceptor, A (MoS_2), phases induced by an increase of the surface acidity of the layer that separated D and A [16]. Synergism via Hso in stacked beds of Ru//Mo, Rh//Mo, Pd//Mo and Pt//Mo has also been demonstrated [17]. The results of these studies clearly indicated that the synergy in HDS over conventional Co(or Ni)Mo catalysts is not necessarily associated uniquely to the formation of Co(Ni)–Mo–S type structures. Obviously, in such physically separated double-bed catalyst configurations, no direct interaction between the promoter and the Mo occur, so the formation of a Co(Ni)–Mo–S type structure can be unequivocally excluded. The observed synergetic effect can only be accounted for by spillover hydrogen. It was further demonstrated that the synergism via Hso observed over double-beds like Co(or Ni)/γ-Al_2O_3//SiO_2//Mo/γ-Al_2O_3 in HDS of dibenzothiophene also led to a higher HYD selectivity as compared to that of the Mo/γ-Al_2O_3 single-bed

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Table 1
Pyridine HDN conversion of Mo/γ-Al_2O_3, Ni/γ-Al_2O_3 single beds and Ni/γ-Al_2O_3//SiO_2//Mo/γ-Al_2O_3 stacked beds.

Bed	HDN (%)		
	498 K	523 K	548 K
Ni/Al_2O_3	0	0	0
Mo/Al_2O_3	3.9	5.5	7.2
$Ni/Al_2O_3//SiO_2//Mo/Al_2O_3$	7.0/1.8[a]	8.0/1.50[a]	9.2/1.3[a]

[a] Promotion factor in HDN of Ni//Mo stacked beds.

Table 2
Pyridine HDN conversion of Mo/γ-Al_2O_3, Ni/γ-Al_2O_3 single beds and Ni/γ-Al_2O_3//SiO_2//Mo/γ-Al_2O_3 stacked beds at 498 K.

Systems	Conversion (%)	Product formation	
		Piperidine	n-pentane
Ni/Al_2O_3	0	–	–
Mo/Al_2O_3	3.9	–	3.9
$Ni/Al_2O_3//SiO_2//Mo/Al_2O_3$	7.0	0.45	6.6

system [18]. In view of the above results on separated stacked-bed experiments, and in order to develop more understanding of the synergisms observed with HYD catalyst configurations, here we extend our investigations from hydrodesulfurisation (HDS) to hydrodesnitrogenation (HDN) reactions. Additionally, changes in the selectivity of the pyridine HDN by influence of Hso are also studied.

2. Experimental

2.1. Catalysts preparation

The monometallic catalyst samples employed in the present study were Mo/γ-Al_2O_3 and Ni/γ-Al_2O_3 monometallic samples prepared by wet impregnation, dried overnight at 373 K and calcined at 823 K for 4.0 h. Nickel nitrate (Merck PA) and ammonium heptamolybdate (Merck PA) were used as precursors. The support was a γ-Al_2O_3 Girdler T-126 (N_2 BET 190 $m^2\,g^{-1}$ and pore volume 0.365 $cm^3\,g^{-1}$) and the separator of both beds was SiO_2 BASF D11-10 (BET 154 $m^2\,g^{-1}$ and pore volume 0.270 $cm^3\,g^{-1}$). The metallic contents of Ni and Mo were 3.9 and 11.9 g of NiO and MoO_3 per 100 g of γ-Al_2O_3, respectively.

2.2. Activity measurements

The pyridine HDN was carried out in a stainless steel continuous-flow microreactor. A sample of 0.2 g Ni/γ-Al_2O_3 and 0.2 g of Mo/ γ-Al_2O_3 of catalyst diluted 1:1 with SiO_2 was used in all the tests. These beds were separated by 2 mm of SiO_2. The composite beds are indicated as Ni/γ-Al_2O_3//SiO_2//Mo/γ-Al_2O_3 and the promotion factor (PF) was calculated as: $((\%\ \text{conversion})_{\text{Ni//Mo stacked beds}})/(\%\ \text{conversion}_{(\text{Ni}+\text{Mo})})_{\text{simple bed}}$. HDN conversions were defined as percent of total nitrogen, removed from the initial gas-oil: $HDN=((N_0-N)/N_0)*100$ (N_0 = initial nitrogen concentration and N = nitrogen concentration after the reaction). The remaining space in the reactor was filled with SiC particles. The particle size of all catalysts, SiO_2 and SiC, was between 0.42 and 0.85 mm. Prior to the reaction, the catalysts received an in situ sulfidation with H_2/H_2S (10%) to 525 K for 4 h. The reaction temperatures were 498, 523 and 548 K; the total pressure was 3 MPa; the liquid feed of 5650 ppm of pyridine (1000 ppm pf nitrogen) dissolved in decaline; and, the liquid hourly space velocity (LHSV) was 30 h^{-1} and H_2 GHSV = 3600 h^{-1}. Samples were analysed by GC with a FID (autosystem XL, Perkin Elmer) equipped with a CPSIL-5 CB column. In addition to unreacted pyridine, piperidine and n-pentylamine were the only products detected.

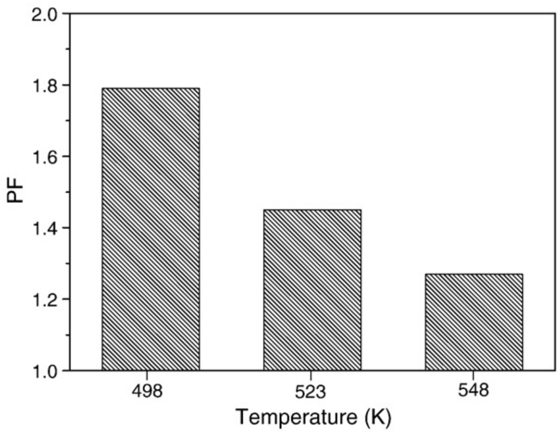

Fig. 1. Promotion factor (PF) in the HDN over and Ni//Mo stacked bed at different reaction temperatures.

Gas-oil enriched with pyridine HDN conversion was performed using the same experimental conditions as described above, except the differences that are summarized below: 0.4 g of Ni/γ-Al_2O_3 and 0.1 g of Mo/γ-Al_2O_3 monometallic catalysts, diluted 1:1 with SiO_2 were used. Prior to the reaction, the catalysts received an in situ sulfidation treatment during 4 h, at 623 K, total pressure 3 MPa, using 7% CS_2 dissolved in gas-oil. The reaction temperatures were 598, 623 and 648 K. The nitrogen content in gas-oil was enriched up to 2000 ppm incorporating pyridine to the initial gas-oil. Total nitrogen was analyzed on an Antek 703C instrument by chemiluminescence detection. For all tests, a stabilization period of at least 2 h was allowed before the first sample was collected.

3. Results and discussion

Table 1 shows the pyridine conversion over Ni/γ-Al_2O_3 and Mo/γ-Al_2O_3 single beds compared with the Ni/γ-Al_2O_3//Mo/γ-Al_2O_3 stacked bed at different reaction temperatures. The Ni/γ-Al_2O_3 material is not active in the temperature range, but the Mo/γ-Al_2O_3 catalyst exhibits a moderate activity.

However, it can be clearly seen that the HDN conversion of the stacked bed (Ni//Mo) is greater than the sum of the activity of the two single beds (Ni + Mo). This proves that the synergism Ni–Mo via Hso, initially reported for HDS reaction [12], also is present for the HDN reaction. As observed for the HDS reaction [12–17] the synergism via Hso in HDN decreases with the reaction temperature as shown in Fig. 1.

In close agreement with Kaluža et al. [19], the PF values obtained in the present study using stacked bed in the HDN are lower than the values obtained previously in the HDS, using similar experimental conditions [15]. Certainly in the model reaction HDN of pyridine

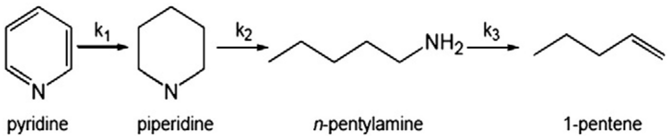

Fig. 2. Reaction scheme for HDN of pyridine.

Table 3
Gas-oil enriched with pyridine HDN conversion of Ni/γ-Al_2O_3, Mo/γ-Al_2O_3 single beds and Ni/γ-Al_2O_3//SiO_2//Mo/γ-Al_2O_3 stacked beds.

Bed	HDN (%)		
	598 K	623 K	648 K
Ni/Al_2O_3	1.0	1.5	3.5
Mo/Al_2O_3	0.5	1.5	3.5
$Ni/Al_2O_3 + Mo/Al_2O_3$	1.5	3.0	7.0
$Ni/Al_2O_3//SiO_2//Mo/Al_2O_3$	2.5/1.7[a]	4.5/1.5[a]	7.5/1.1[a]

[a] Promotion factor of Ni//Mo in stacked bed.

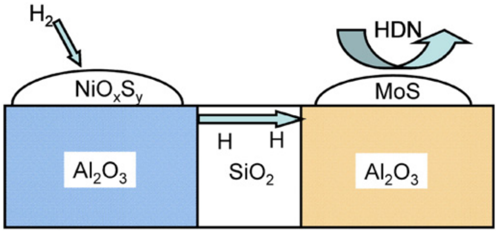

Fig. 3. Schematic drawing representing the promotional effect of Ni_XS_Y provoked hydrogen spillover, activating the physically separated Mo/Al_2O_3 sites for the HDN reaction.

simultaneous with HDS of thiophene, Kaluža et al. [19] find a PF of 5.7–4.6 in the HDS and 1.8–1.6 in the HDN over NiMoS catalyst.

Table 2 shows the product formation in the pyridine conversion over Ni/γ-Al_2O_3, Mo/γ-Al_2O_3 and Ni//Mo at 498 K. As seen, n-pentane is the only reaction product from the Mo/γ-Al_2O_3 catalyst, while Ni/γ-Al_2O_3//Mo/γ-Al_2O_3 presents n-pentane and piperidine as reaction products. Sonnemans et al. [20] claim that the pyridine is first hydrogenated to piperidine, and then further on to pentylamine by C–N bond cleavage. Finally the pentylamine is transformed to 1-pentene by a second C–N bond cleavage, as shown in Fig. 2.

The formation of piperidine in the stacked Ni//Mo bed suggests that Hso promotes the hydrogenation of the pyridine. This behavior is in close agreement with the results obtained in the HDS of DBT [18] in which Hso modified the active sites by increasing the amount of hydrogenation sites rather than the hydrogenolisis sites of the MoS_2.

The HDN results of gas-oil enriched with pyridine by Ni/γ-Al_2O_3 and Mo/γ-Al_2O_3 monometallic bed catalysts, as well as the stacked-bed configuration, are summarized in Table 3. The Ni/γ-Al_2O_3 and Mo/γ-Al_2O_3 monometallic catalysts both exhibit some activity for the gas-oil HDN under the experimental conditions employed. However, also for the HDN reaction of gas-oil a clear synergism between Ni/γ-Al_2O_3 and Mo/γ-Al_2O_3 in separated beds is observed, since the activity of the Ni/γ-Al_2O_3//SiO_2//Mo/γ-Al_2O_3 system is higher than the sum of the Ni/γ-Al_2O_3 and Mo/γ-Al_2O_3 systems. Though the activities and Fso in Tables 1 and 3 obviously cannot be compared directly to the pyridine results, the Fso tendencies are similar. The promotion factor decreases when the reaction temperature increases, as was also repeatedly observed in all earlier work with the HDS reaction [12–17].

4. Conclusions

These present results clearly indicate that the previous conclusions about the hydrogen spillover action, observed for various transition metal based catalysts for the HDS reaction are in fact also present, and appear to be a general behaviour for the HDN reaction as well, as depicted in Fig. 3. However, the Hso activated MoS-sites are more active for the HDS reaction than for the HDN reaction.

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