Synergy between Mo/SiO$_2$ and Co/SiO$_2$ beds in HDS: a remote control effect?

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Synergy between beds of Mo/SiO$_2$ and Co/SiO$_2$ separated by 5 mm of SiO$_2$ in the hydrodesulfurization (HDS) of gas oil, carried out in a high-pressure continuous-flow micro-reactor, was demonstrated.

Unsupported hydrodesulfurization (HDS) catalysts consist of mixtures of MoS$_2$ or WS$_2$ and Co$_9$S$_8$, NiS, FeS$_x$, or RuS where synergism occurs. In mechanical mixtures (MM), prepared by the comaceration procedure, synergism has been explained by the remote control (RC) model developed by B. Delmon *et al.*,[1–7] for the case where no new phase is formed. In this model the synergism is related to a hydrogen spillover species (Hso), which migrates from a donor phase (D = Co$_9$S$_8$, NiS, FeS$_x$ or RuS) to an acceptor phase (A = MoS$_2$ or WS$_2$) and gives RC. The difficulty with total acceptance of the RC model has been that in MM the formation of a new phase cannot be totally excluded. When mixtures are prepared by a homogeneous simultaneous precipitation procedure, synergism has been explained by the existence of a new although unstable[8,9] phase designed as "Co–Mo–S", a theory developed by Topsoe *et al.*[10]

Studies of Hso diffusion coefficient,[11–13] Hso transport,[14,15] and Hso migration using membranes,[16] carried out at low pressures and ideal conditions, have shown that the hydrogen migration distance ranges from nm to several cm distances.[17] Consequently, for HDS it is necessary to demonstrate under operating conditions[18] if Hso migrates from D to A phase. Thus, the aim of this study is to show that synergism between separated beds of Mo/SiO$_2$ and Co/SiO$_2$ occurs, and see whether it can be explained by a mechanism due to Hso (or: *the RC model through Hso*).

The catalytic measurements for HDS of gas oil were carried out in a high-pressure continuous-flow micro-reactor.[19] Prior to reaction, the catalysts were sulfided with 7 vol% CS$_2$–gas oil mixes at 350 °C and 3.0 MPa total pressure for 4 h. The feed for HDS was a commercial gas oil, containing 470 mg kg^{-1} of S. The performance of the catalysts was determined in the 325–375 °C temperatures range under standard conditions (3.0 MPa total pressure, 9 h^{-1} liquid hour spatial velocity, 3600 h^{-1} gas hour spatial velocity, and H$_2$/feed ratio of 400). Under these conditions the reaction is not controlled by mass transfer phenomena.[20] In all tests, a stabilization period of at least 2 h was allowed before the first sample was collected; three samples were collected at each reaction temperature. Total sulfur in each sample was determined by iodometric titration of SO$_2$ using a LECO analyzer. The HDS conversion was defined as percent of the total sulfur removed from the initial gas oil: HDS = $(S_0 - S)/S_0 \times 100$.

The Co/SiO$_2$ and Mo/SiO$_2$ samples were prepared by impregnation in a rotary evaporator, dried at 110 °C, and calcined at 550 °C for 0.5 h.[19,21] Cobalt nitrate (Merck p.a.) and ammonium heptamolybdate (Merck p.a.) were used as precursors, and SiO$_2$ (BASF D11-10, 80 m^{2}g^{-1}) was used as support. Two samples, containing respectively 2 g of CoO or 8 g of MoO$_3$ per 100 g of SiO$_2$, were prepared.

Five tests were carried out (Table 1). A 1 g portion of each individual sample was used in Test No. 1 and 2. The remaining space in the reactor was filled with SiC particles, as in the following tests. The "composite bed" tests (Test No. 3 and No. 4) were carried out as follows:

a) In Test No. 3 a three-layer system was prepared. The first bed diluted 1 g of Co/SiO$_2$ and the second 1 g of Mo/SiO$_2$, diluted 1 : 1 vol/vol with SiO$_2$ to optimize hydrodynamics. Both beds were separated by a 5 mm (1 g) of SiO$_2$. This "composite bed" was indicated as Co/SiO$_2$//SiO$_2$//Mo/SiO$_2$.

b) In Test No. 4 the same amounts but located in the opposite position compared to Test No. 3 were used: Mo/SiO$_2$//SiO$_2$//Co/SiO$_2$.

One mixed bed was also prepared by mixing 1 g of Co/SiO$_2$ and 1 g of Mo/SiO$_2$ (Test No. 5), and represented as Co/SiO$_2$ + Mo/SiO$_2$.

Table 1 indicates that HDS conversion obtained with Co/SiO$_2$//SiO$_2$//Mo/SiO$_2$ composite bed (Test No. 3) is much higher than those obtained with Co/SiO$_2$ (not active in HDS under our experimental conditions) and Mo/SiO$_2$ (Test No. 2), showing that synergism occurs. Considering that in Test No. 3 contact between the Mo/SiO$_2$ and Co/SiO$_2$ beds can be excluded, results unequivocally demonstrate, under operating conditions, that the synergism is mainly a consequence of a remote control phenomenon. Thus, the migration of Hso from Co$_9$S$_8$ (D) to MoS$_2$ (A) over distances longer than 5 mm occurs in our experimental conditions.

According to the RC model, to achieve synergy, the Hso must migrate from Co/SiO$_2$ to Mo/SiO$_2$ beds. The differences in HDS (%) between Test No. 2 and No. 4 are within experimental error, indicating that under the experimental design used in Test No. 4 no synergism takes place. This result suggests that the Hso concentration gradient[17] between the D and A phases in not enough to promote synergism through its migration from the bottom to the upper part of the micro-reactor. The low or non-existing effect in test No. 4 suggests too that H$_2$S produced upstream on Mo inhibits Hso migration on SiO$_2$.

To improve the proximity between D and A, Test No. 5 was carried out. With this mixed bed the HDS activity is even higher than with Test No. 3 (Table 1), opening unlimited possibilities to study nanomaterials as supports, as suggested by Delmon.[18]

The "synergism ratio" (SR, defined as "HDS (%) in the presence of Hso/HDS (%) in the absence of Hso") decreases when the reaction temperature increases (Table 2). When the reaction temperature increases, the production of Hso decreases, probably because less Hso remains attached to the surface. This over-compensates the increase of the rates of formation and migration of Hso. This has been observed in other

Table 1 HDS conversion of Co/SiO$_2$ and Mo/SiO$_2$ beds

		HDS (%)		
Test No.	Bed	325 °C	350 °C	375 °C
1	Co/SiO$_2$	0	0	0
2	Mo/SiO$_2$	8.0	16.8	29.1
3	Co/SiO$_2$//SiO$_2$//Mo/SiO$_2$	13.6	25.3	40.2
4	Mo/SiO$_2$//SiO$_2$//Co/SiO$_2$	8.3	18.0	30.4
5	Co/SiO$_2$ + Mo/SiO$_2$	30.6	35.1	40.0

Table 2 Dependence of the "synergism ratio" with the reaction temperature

"Synergism ratio"	325 °C	350 °C	375 °C
HDS (Test No. 3/Test No. 2)	1.7	1.5	1.4
HDS (Test No. 5/Test No. 2)	3.8	2.1	1.4

reactions where RC operates.[11–17] Thus, the lower the Hso production, the lower the activation of the catalytic centers and consequently the synergism ratio.

In conclusion, a simplified experimental design showed a synergism between separated beds of Mo/SiO_2 and Co/SiO_2, which can be explained by the remote control model through a migration of hydrogen spillover, even working under operating conditions.

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