ACTIVATION OF HYDROGEN OVER SULFIDE CATALYSTS. RELEVANCE TO KINETICS AND MECHANISMS OF HYDROTREATING REACTIONS.

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Introduction
The regulations on transportation fuels regarding sulfur content in particular are more and more severe. This forces the refiners to achieve what is commonly called deep desulfurization. One of the consequences of this requirement is that the demand in the refinery regarding hydrogen is increasing drastically. This is made all the more crucial as at the same time the tendency is to reduce the amount of aromatics in gasoline and consequently the capacity of the reforming units which provide hydrogen in the refinery.

Another reason why it is essential to better understand hydrogen activation on hydrotreating catalysts and the hydrogenation properties of these catalysts is related to the HDS of FCC gasoline in which the objective is to obtain high sulfur removal with a minimum of olefin hydrogenation.

Twenty years ago, Barbour and Campbell [1] reported the results of the hydrogenation of buta-1,3-diene on a D$_2$S-treated MoS$_2$ catalyst. They concluded that hydrogen present as SH groups on the surface was involved in the hydrogenation of the diene, which could suggest that the dissociation of H$_2$ was heterolytic. Later on, in their theoretical approach of the homolytic and heterolytic dissociation of H$_2$, Anderson et al. [2] concluded that the most stable chemisorption form of hydrogen was heterolytic at edges of MoS$_2$ crystals. Since then the authors of numerous studies have assumed that the dissociation of hydrogen on sulfides was heterolytic [3-8].

In a recent review, Furimsky et al. [9] examined in detail the reaction of sulfide surfaces with hydrogen and in particular the mechanism of creation of vacancies as well as the nature of the species resulting from the chemisorption of hydrogen. The purpose of this contribution is not to cover all the aspects of the interaction of hydrogen with sulfides, it will focus mainly on the dissociation of H$_2$. We will review a number of experimental results which are in favor of the heterolytic dissociation of hydrogen and show its relevance to mechanisms and kinetics of hydrotreating reactions. We will also report examples of promoter effects related to hydrogen activation and to the hydrogenation of olefins.

Tracer experiments on the dissotiation of hydrogen on sulfides
To our knowledge no direct proof of the heterolytic dissociation of H$_2$ over MoS$_2$ catalysts has been reported yet. However quite a number of experimental facts obtained by various authors are clearly in favor of such a dissociation mode.

Isotopic exchange experiments between H$_2$ and D$_2$.S. The experiments were carried out at 80°C on NiMo/Al$_2$O$_3$ catalyst samples which were presulfided with a H$_2$/H$_2$S mixture (10 vol.% of H$_2$S) at 400°C [10].

The formation of HD indicated that isotopic exchange occurred between H$_2$ and D$_2$. Similar results were obtained by Hensen et al. on carbon supported catalysts [11]. Hence, we can suppose that both reactants dissociate in the same manner on the same kind of catalytic centers. If we assume as it is generally accepted that the dissociation of H$_2$S (D$_2$S) on sulfides is heterolytic [2,4,12-18], we can suppose that the chemisorption of hydrogen also is heterolytic.

Involvement of support hydrogen in the isotopic exchange between gas phase H$_2$ and D$_2$. By carrying out H$_2$-D$_2$ exchange experiments on a H$_2$/H$_2$S presulfided NiMo/Al$_2$O$_3$ catalyst or by reacting D$_2$ on such a catalyst sample, it was shown through isotopic delution that gaseous D$_2$ could incorporate H-atoms coming from the support [10,19,20]. On a typical commercial catalyst, the amount of support hydrogen which could be incorporated into the deuterium of the gas phase varied depending on the pretreating conditions and could be as high as 90% of the hydrogen held by the solid after sulfidation. It was also shown that the latter resulted mostly from the adsorption of H$_2$S [20]. Since the isotope exchange between H$_2$ and D$_2$ is extremely slow under the same conditions with the pure alumina support, it was concluded that the hydrogen held by the support could only exchange with gas phase hydrogen via the sulfide through a spillover-like process. This was confirmed by FTIR experiments [19,20] which showed that OD bands (2640 cm$^{-1}$) appeared readily on the alumina support of a presulfided NiMo/Al$_2$O$_3$ catalyst during its exposure to D$_2$ while OH bands (3580 cm$^{-1}$) disappeared. This process barely existed on the pure presulfided support under the same conditions.

Since the H atoms of the hydroxyl groups of the alumina support have undoubtedly an ionic character, this is also good evidence in favor of the heterolytic splitting of D$_2$ (H$_2$).

Incorporation of deuterium from D$_2$S in propane via propene hydrogenation. The hydrogenation of propene over a D$_2$S-treated NiMo/Al$_2$O$_3$ catalyst showed that D-atoms from D$_2$S were involved in the reaction [21]. This is in accordance with the results reported previously by Barbour and Campbell [1] regarding the hydrogenation of buta-1,3-diene over a D$_2$S-treated MoS$_2$ catalyst although it is difficult at the moment for us to conclude, as these authors did for butadiene, that D-atoms were incorporated directly from D$_2$S to propene.

Relevance of the heterolytic dissociation of hydrogen to reaction mechanisms and kinetics
The heterolytic dissociation of H$_2$ on a catalytic center composed of a sulfur vacancy located on a molybdenum atom and of a neighbouring sulfur anion leads to the H-atom having a hydride character adsorbed on the metal ion and the H-atom with a protonic character adsorbed on the sulfur anion [3-6]. However, as shown recently by DFT calculations [22], the hydride bound to the metal seems to be highly unstable with Molybdenum-based catalysts, especially with nickel-molybdenum. Contrary to what was obtained recently by DFT calculations [22], the hydride bound to the metal seems to be highly unstable with Molybdenum-based catalysts, especially with nickel-molybdenum. Contrary to what was obtained with ruthenium catalysts [18], metal-hydrogen species have not been observed yet. H$_2$S is supposed to dissociate in the same manner with its proton adsorbed on a sulfide anion and the sulhydryl group on the metal; this leads to two SH groups.

The first step of the hydrogenation of unsaturated substrates can be either the addition of H$^+$ or of H$. Kinetic modeling studies bring some information on this point [6,7,23].

In their study of the effect of H$_2$S on the hydrogenation of toluene over a Mo/Al$_2$O$_3$ catalyst, Kasztelan and Guillaume [6] compared various kinetic models supposing molecular, homolytic and heterolytic dissociative adsorption of H$_2$ and H$_2$S. By computing the rate laws according to the classical Langmuir-Hinshelwood-Hougen-Watson method, they came to the conclusion that the model which fitted at best the kinetic orders of the reaction with respect to the various reactants, especially H$_2$S, was the one supposing the heterolytic dissociation of H$_2$ and H$_2$S on a vacancy and a sulfur anion. The hydrogenation was found to proceed via addition of a hydride followed by the addition of a proton to the aromatic molecule. The changes in kinetic order with respect to H$_2$S was
explained by supposing that the rate-limiting step of the reaction was changing from one of these two elementary steps to the other as the H$_2$S partial pressure increased.

More recently, Blanchin et al. [23] have used the Chemkin/Surface Chemkin II tool to investigate the effect of H$_2$S and of NH$_3$ on the same reaction catalysed by a NiMo/Al$_2$O$_3$ catalyst. They found also that the model involving the heterolytic dissociation of H$_2$ and H$_2$S on centers composed of an unsaturated molybdenum ion and of a sulfur anion fitted at best with the experimental data. They confirmed that the hydrogenation of the aromatic molecule started with the addition of a hydride followed by the addition of a proton, the latter being the rate-limiting step of the reaction in the range of H$_2$S partial pressures investigated. However the rate-limiting character of this step depended very much on the partial pressure of H$_2$S which in addition to H$_2$ provides protons to the system.

Orozco and Vrinat used the same approach as Kasztelan and Guillaume to investigate the effect of H$_2$S on the hydrodesulfurization of dibenzothiophene through kinetic modeling [7]. Like Kasztelan and Guillaume, they concluded that the reaction involved the heterolytic dissociation of H$_2$ and H$_2$S and that depending on the partial pressure the rate-limiting step of the reaction could be the addition of a hydride ion to the adsorbed substrate or the attack of a dihydrointermediate by a sulfur anion to achieve carbon-sulfur bond cleavage.

Promoter effects in hydrogen activation and in the hydrogenation of olefins.

The role of the promoters in the hydrogenation process on sulfides was investigated by measuring the effect of cobalt and nickel on the activities of MoS$_2$–based catalysts in the isotopic exchange between H$_2$ and D$_2$ and in the hydrogenation of cyclopentene in the absence of H$_2$S [24]. The catalyst samples containing the same amount of molybdenum and various quantities of cobalt or nickel were presulfided with a H$_2$/H$_2$S mixture (10 vol.% of H$_2$S) at 400°C then treated at 350°C under helium for 1 hour. Under these conditions, the catalysists containing cobalt were much more active than those containing nickel in the H$_2$-D$_2$ isotopic exchange reaction so that the experiments were carried out at 35°C with the former and 80°C with the latter [20]. It was verified that both series of catalysts exhibited the expected synergy effect in the hydrodesulfurization of dibenzothiophene at 340°C under 30 bar of hydrogen [25]. However no synergy effect was obtained with nickel in the isotopic exchange between H$_2$ and D$_2$ while the catalyst containing cobalt with a Co/Co+Mo atomic ratio of 0.3 was found five times more active than the unpromoted catalyst. This is in accordance with other results reported in the literature [11,26,27] and was interpreted by Travert et al. by a difference in the rate-limiting step of the process [22]. Surprisingly, the reverse was obtained regarding the promoting effect in the hydrogenation of cyclopentene. The promoting effect of cobalt (2 only for a Co/Co+Mo atomic ratio of 0.3) was much weaker than the effect of nickel (about 10 for the same atomic ratio).

While both promoters have similar effects in hydrotreating reactions as well as in the thioeducation of ketones [25], their effect on hydrogen activation and on the hydrogenation of olefins seem to be different. This might be a question of operating conditions but also of kinetics [22] regarding hydrogen activation and hydrogenation or of sulfur coverage connected to the intrinsic properties of the solids.

Conclusions

Various observations (the isotopic exchange between H$_2$ and D$_2$S, the contribution of the support to the isotopic exchange between H$_2$ and D$_2$) as well as theoretical calculations are definitely in favour of the heterolytic dissociation of hydrogen on sulfides. The best fittings regarding the kinetic modeling of hydrotreating reactions is also obtained when supposing such a dissociation process.

However certain observations like differences in promoting effects with cobalt and nickel in hydrogen activation and hydrogenation have to be rationalize and further experiments are needed.

References

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