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Study of the sulfidation process of CrO_3–Al_2O_3 hydrodesulfurization catalysts by a ^{35}S-labeled H_2S pulse tracer method

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Abstract

Sulfidation of CrO_3–Al_2O_3 catalysts (11.1, 16.6 and 22.2 wt.% CrO_3) synthesized by incipient wetness impregnation method was monitored by a ^{35}S radioisotope ($[^{35}S]H_2S$) pulse tracer in situ method. This original method permitted us a better understanding of these relatively poorly documented catalytic systems. Experiences confirmed that, in a first step, for temperatures inferior to 400 °C, CrS_x species are progressively formed. Then, in a second step for a temperature near 400 °C, formation of Cr_2S_3 entities is achieved, leading to their decomposition into CrS. This showed that the catalytic phase morphology depends drastically on the sulfidation temperature. Moreover, it was found that the increase in DBT activity with the Cr content previously observed was due to a modification of the nature of the active phase and not to an increase in its quantity. Indeed, whilst the sulfur quantity that accumulated on the catalysts containing 11.1 and 22.2 wt.% CrO_3 was almost the same, the DBT HDS activity of the latter was ∼50% higher.

Keywords: Hydrodesulfurization; Cr; Alumina; ^{35}S; Sulfidation

1. Introduction

Although the use of chromium as a catalyst is well documented for various reactions, there are only a few examples of papers dealing with its use for hydrodesulfurization (HDS) or hydrodenitrogenation (HDN) [1]. Examining the literature, one finds that the results appear to be quite contradictory. Indeed, whilst Pecoraro and Chianelli [2] found that the activity of unsupported Cr_2S_3 was much lower than that of unsupported MoS_2, Lacroix et al. [3] found that, whilst the activities were significantly lower than that observed for WS_2, the activity observed on Cr_2S_3 was almost reaching the one observed on MoS_2. In the case of carbon-supported catalysts, whilst Vissers et al. [4] found that HDS of thiophene activity was higher in the presence of Cr than in the presence of Mo or W, Ledoux et al. [5] observed that the use of Mo gave better results than the use of Cr. Nevertheless, these Cr, Mo and W loadings were different so that a direct comparison of the results is quite difficult. Concerning the HDN of quinoline [6,7], activity was found to be lower in the case of Cr than in the case of

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Mo. The reverse was observed for the HDN of decahydroquinoline [8]. In a recent study, HDS of DBT was carried out on Cr, CrCu, CrNi and CrCo alumina supported catalysts [9]. It was found that the activity increases in the order of Cu–Cr $\leq$ Cr $<$ Co–Cr $<$ Ni–Cr, this order being correlated with the amount of labile sulfur (investigated using a ^{35}S radioisotope in situ pulse tracer method). Other authors showed also that the presence of weak sulfur bonds are required to form catalytic sites [10–12]. Therefore, the more the chromium–sulfur bond strength decreases, the more the number of labile sulfur atoms increases, leading to an increase in the number of active sites, i.e. an increase in activity. In brief, according to the literature, it appears that the activity of Cr catalysts is dependent on either the use or not of a carrier, the nature of the carrier and the nature of the selected catalytic reaction. We will show in this work that the sulfidation temperature also plays a very important role in determining the nature of the supported catalytic phase.

We decided to study Cr-based catalysts because its use can give some advantages, even though only a few examples of attempts at using chromium as an HDS catalyst are found in the literature, such as Cr/Al_2O_3 catalysts [13], Cr–Mo/Al_2O_3 catalyst [14], chromium-exchanged Y Zeolite [15], and chromium-pillared clays [16,17]. Indeed, chromium is not only cheap, but is also a small atom, which can be loaded on supports in high proportions to achieve better catalytic activities (in the case of Mo-based catalysts, it is well known that up to the dispersion limit, HDS catalytic activity increases with the active metal content). Moreover, selection of a proper promoter, like in the case of Mo- or W-based HDS catalysts, can increase drastically the performances of Cr-based catalysts [13].

Due to the relative lack of data on chromium catalysts, we decided to investigate the behavior of Cr-Al_2O_3 supported catalysts upon the sulfidation stage by a ^{35}S radioactive pulse tracer method (^{35}S RPTM), based on a method developed by some of the present authors. In a previous study [9], we prepared a series of CrO_3–alumina catalysts using different CrO_3 loadings and we tested them in HDS reaction of DBT. We found that an increase in Cr loading was accompanied with an increase in activity. Moreover, DBT HDS tracer experiments showed that when the Cr loading increased, the number of labile sulfur species increased. Nevertheless, it is also important to check how the total number of sulfur species accumulated on the catalysts varies with the Cr loading. This allows one to determine if the increase in detected labile sulfur species is only linked with the development of the active phase (i.e. giving a linear relation between the number of total labile sulfur species and the total sulfur uptake during the sulfidation process), or is also due to a modification of the nature of the active phase. The method used in the present paper allowed us to measure the quantity of sulfur accumulated on the catalysts during the presulfidation stage and also to specify the genesis process of the active phase during the sulfidation of CrO_3-supported catalysts. The clarified knowledge of this relatively simple system gave precious information for the understanding and the development of more complicated systems based on Cr deposited on alumina, such as the doped catalysts described above.

2. Experimental

2.1. Chemicals

Chromium nitrate $Cr(NO_3)_3{\cdot}9H_2O$ was purchased from Wako Chemicals. Hydrogen (99.99%) and nitrogen (99.99%) were supplied by Tohei Chemicals. ^{35}S-labeled hydrogen sulfide ($[^{35}S]H_2S$) was prepared as follows: to obtain ^{35}S-labeled sulfur, a commercially available toluene solution of ^{35}S (total radioactivity: 7 MBq, Amersham Co., Ltd.) was mixed up with 7 g of sulfur (^{35}S) and then the toluene of the mixture was removed in vacuum. This ^{35}S-labeled sulfur (7 g) was charged into an autoclave (500 ml). After H_2 purge, the autoclave was pressurized to $40\,kg\,cm^{-2}$ with H_2 before being heated at a rate of $5\,^{\circ}C\,min^{-1}$ and was kept at 430 °C during 30 min. The autoclave was then rapidly cooled down to room temperature. Obtained $[^{35}S]H_2S$ was mixed with H_2 in order to obtain ∼25% of $[^{35}S]H_2S$ in H_2. Real concentration in the autoclave was measured by gas chromatography and was found to be ∼23.6%.

2.2. Catalysts

The CrO_3–Al_2O_3 catalysts used in this study were prepared by a conventional incipient wetness impregnation method: a γ-Al_2O_3 supplied from Nippon Ketjen (248 $m^2\,g^{-1}$, 0.712 $ml\,g^{-1}$) was impregnated with an aqueous solution of chromium nitrate hydrate and then dried at 120 °C for 3 h before being calcined in air at 450 °C for 15 h. Three catalysts with different Cr loadings were prepared: 11.1, 16.6 and 22.2 wt.% (CrO_3 wt.%). They were, respectively, called Cr11.1, Cr16.6 and Cr22.2.

2.3. ^{35}S radioisotope pulse tracer method

2.3.1. Sulfidation of supported oxides

In order to investigate the sulfidation process, a ^{35}S radioisotope pulse tracer sulfiding method was used [18]. Apparatus is shown in Fig. 1. The sulfidation reactions were conducted under atmospheric pressure in a fixed bed reactor (Pyrex glass). Before experiments, catalysts were dried overnight under a flow of N_2 at 420 °C and then cooled down to room temperature. Catalysts (0.1 g) were then slowly heated to the desired temperature. After 30 min (time needed to obtain temperature equilibrium), a pulse of $[^{35}S]H_2S$ was introduced into the gas sampler (2.46 ml). One minute later (after stabilization), the pulse was transferred to the reactor. The radioactive products released from the reactor were trapped in a bubbler containing an absorbing solution of Carbosorb during 9 min. Then, the next $[^{35}S]H_2S$ pulse was introduced in the gas sampler. The radioactivity of $[^{35}S]$ trapped in Carbosorb was measured by a liquid scintillation counter, as described elsewhere [19–23]. The introduction of $[^{35}S]H_2S$ pulses was repeated until the count value detected by the radioanalyzer became stable at a value equal to that of one introduced pulse. Two distinct experimental procedures were followed. In the first one, sulfidation state was checked at 100, 200, 300, and 400 °C, these temperatures being reached at a rate of 3 °C min^{-1}. At each temperature, measurements started after a stabilization time of 30 min. The second experimental procedure was performed directly at 400 °C, without measuring the amount of sulfur accumulated on the catalysts at intermediate temperatures. The sample investigated according to this latter experimental procedure was noted Cr22.2(S400). A flow of N_2 (30 ml min^{-1}) was maintained in the experimental apparatus, whatever the experiment.

2.3.2. Re-oxidation of supported sulfides

To confirm the amount of sulfur incorporated into the catalysts, the previously sulfided catalysts were oxidized with oxygen. After completion of the selected sulfidation procedure, the samples were heated at 450 or 500 °C in a nitrogen stream (30 ml min^{-1}). Then, the carrier gas was replaced by oxygen gas. The

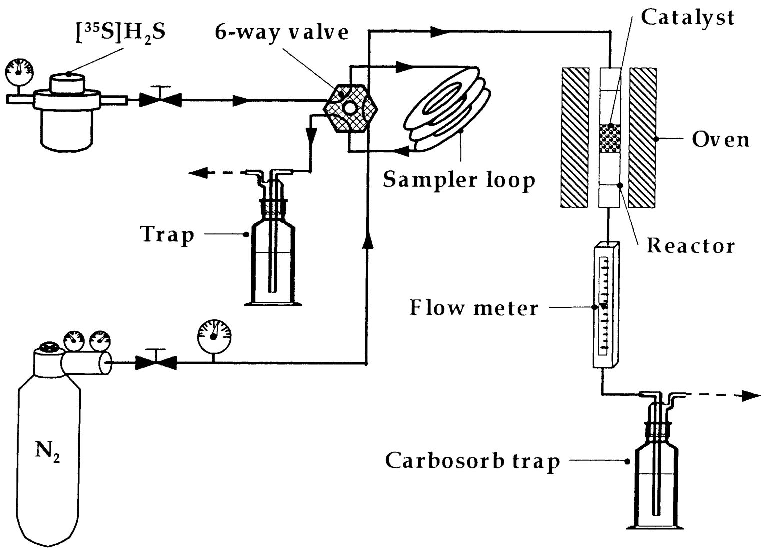

Fig. 1. Illustration of the ^{35}S pulse tracer apparatus.

oxygen was introduced at a flow rate of 30 ml min^{-1} during 1.5 h. Sulfur oxides eluted from the catalysts were adsorbed by a molar NaOH aqueous solution. The total radioactivity of the sulfur oxides eluted from the catalyst was measured by the liquid scintillation counter in the same way as that described for the sulfidation.

3. Results

A typical result obtained for the Cr16.6 catalyst is presented in Fig. 2. At each temperature, detected radioactivity increases when the number of pulse increases, up to recovering a value equal to the one measured for the introduced pulse (i.e. introduced pulse is entirely recovered without S accommodation on the catalyst surface). This indicates that the catalyst is progressively "saturated," i.e. it reaches its maximum sulfidation state under the experimental conditions, and therefore cannot accommodate any more sulfur. Whilst for 100, 200 and 300 °C, the observed tendency was similar, for some of the first pulses at 400 °C, the detected radioactivity was higher than that of one introduced pulse. Moreover, yellowish particles coming out from the reactor, which were thought to be elemental sulfur S_8, were clearly observed from 200 °C. A great part of them were carried off to the trap by the N_2 flow. After the measurement at 400 °C, some S_8 remaining on the glass parts of the experimental apparatus was collected and its quantity and radioactivity were respectively measured by a balance and by the scintillation counter, as described in the experimental section. Black boxes in Fig. 2 represent the collected radioactivity during the temperature increase between two experimental temperatures (in the case of 400 °C, it represents the radioactivity collected during the rise of temperature before the re-oxidation experiment plus the normalized radioactivity of the S_8 collected in the experimental apparatus).

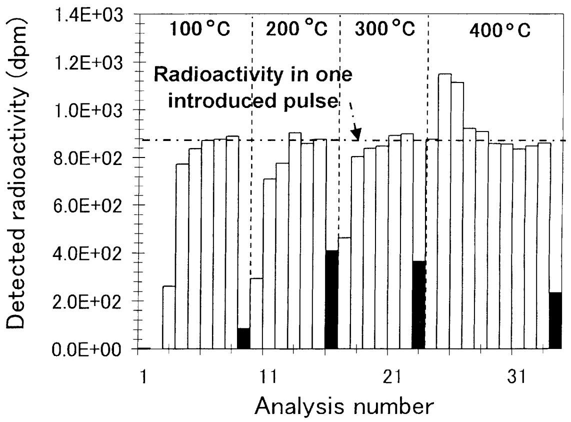

Fig. 2. ^{35}S pulse tracer experiment result for Cr16.6. Black rows represent radioactivity collected during the temperature increase.

The results obtained for all the experiments are reported in Table 1. At each temperature, the amount of S accumulated on the catalyst was deduced from the results like the ones presented in Fig. 2 by calculation of the difference of introduced and released total sulfur amount. Except for Cr22.2(S400), the amount of sulfur accumulated on the catalyst was almost the same on the catalyst containing 22.2 wt.% CrO_3 and on the one containing 11.1 wt.% CrO_3 whilst the lowest amount was obtained for the 16.6 wt.% CrO_3 catalyst. In all the cases, the total amount of S accumulated on the catalysts at 400 °C was lower than the one at 300 °C. This was explained by the creation and liberation of H_2S (and elemental sulfur S_8) as we will explain in the Section 4. If we compare the results obtained for the 22.2 wt.% CrO_3 catalyst according to both experimental conditions, i.e. direct sulfidation

Table 1
Amount of sulfur accumulated on the catalyst during the sulfidation procedure and the amount of S released during the re-oxidation of the sulfided catalyst

Catalyst	Sulfidation S accumulated on the catalyst (mg g^{-1} catalyst)				Re-oxidation S released from the catalyst (mg g^{-1} catalyst)
	100 °C	200 °C	300 °C	400 °C	450 °C (500 °C in parenthesis)
Cr11.1	24.1	33.8	39.7	29.7	3.9
Cr16.6	21.7	25.7	27.2	21.2	9.7
Cr22.2	28.6	38.7	40.9	30.6	19.8 (32.6)
Cr22.2(S400)	–	–	–	41	25.4 (39.2)

at 400 °C (Cr22.2(S400)) and progressive sulfidation performed at 100, 200, 300 and then 400 °C (Cr22.2), we can see that S amounts accumulated at 400 °C are quite different according to the experimental conditions (with respective values of 41 and 30.6 mg g_{cat}^{-1}).

Re-oxidation of the sulfided catalysts showed that whilst for the catalysts containing 11.1 wt.% CrO_3, the recovered amount of S was very low (only ∼13% at 450 °C), for the 16.6 wt.% CrO_3 catalyst, the re-oxidation percentage increased up to 46% and the result obtained for 22.2% CrO_3 catalysts reached 100% for a re-oxidation temperature of 500 °C (∼65% at 450 °C).

4. Discussion

4.1. Sulfidation mechanism

As a first remark, we gave the Cr loading as CrO_3 wt.% but the real state of Cr on the catalyst oxide precursor is very likely to be Cr_2O_3. Indeed, calcined catalysts exhibited a dark green color, characteristic of the latter compound whilst the former is known to be red. Further, it is well known that Cr_2S_3 can be formed by heating powdered Cr with sulfur, or by the action of H_2S on Cr_2O_3, $CrCl_3$ or Cr. Moreover, Cr_2S_3 was proposed as the most stable chromium sulfide under an H_2/H_2S atmosphere [2]. It decomposes to CrS on being heated, via a number of intermediate phases. Some of these phases can also be progressively formed during the sulfidation of Cr_2O_3. Their sulfur content varies from 0.95 to 1.5 atoms per Cr atom, and we give a brief description of them in Table 2 [24]. Some authors also proposed that Cr_2S_3 decomposition gives a mixture of CrS and $CrS_{1.17}$ [25]. Nevertheless, this latter compound can also be considered as an intermediate compound and is likely to be further reduced into CrS under appropriate experimental conditions.

Table 2
Different phases obtained upon sulfidation of chromium (from [24])

Compound (ideal structure)	Stability domain
CrS	$CrS_{0.95–1}$
Cr_7S_8	$CrS_{1.14–1.15}$
Cr_5S_8	$CrS_{1.17}$
Cr_3S_4	$CrS_{1.27–1.32}$
Cr_2S_4	$CrS_{1.45}$
Cr_2S_3	$CrS_{1.5}$

We supposed that the behavior of Cr supported on alumina is close to the above-described one for unsupported Cr oxide species. Therefore, it is reasonable to postulate that in a first step Cr_2O_3 sulfidation gives progressively Cr_2S_3 through the formation of CrS_x intermediate sulfur compounds (CrS, Cr_7S_8, Cr_5S_6 and Cr_3S_4 are given as possible Cr sulfide compounds [24]). Then, formed Cr_2S_3 is decomposed into CrS in a second step (as further calculations will confirm). Chemical equations can therefore be written as follows:

Sulfidation

$$Cr_2O_3 + 3H_2S \Leftrightarrow Cr_2S_3 + 3H_2O \qquad (1)$$

Decomposition

$$Cr_2S_3 + H_2 \rightarrow 2CrS + H_2S \qquad (2)$$

Global reaction

$$2CrO_3 + 2H_2S + 4H_2 \rightarrow 2CrS + 6H_2O \qquad (3)$$

We only represented the case of the complete reaction into the Cr_2S_3 final product. But in fact, it is supposed to be formed through the progressive intermediate CrS_x species sulfidation, which formulation approaches progressively the one of Cr_2S_3 when conditions are becoming more and more severe (increase of the temperature from 100 to 400 °C). Further, as mentioned before, S_8 formation was also observed but its formation mechanism has not yet been made clear, so that no reliable chemical equation can be proposed.

We will now interpret the sulfur uptake results according to the above equations. We will call X, the amount of Cr impregnated on the catalyst expressed in CrO_3 wt.%, and α, the percentage of sulfidation of Cr_2O_3 into Cr_2S_3. $(M_S)_{Sul}$, the amount of sulfur accumulated on the catalyst (Eq. (1)), is therefore equal to $4.8\alpha X$. That means that sulfidation process leads to the accumulation of $4.8\alpha X$ mg of sulfur ($(M_S)_{Sul}$) on the catalyst (detected by the ^{35}S RPTM).

During decomposition of Cr_2S_3 (Eq. (2)), $(M_S)_{Dec}$, the amount of sulfur released is equal to $1.6\alpha X$ (mg of sulfur). As a consequence, considering only this decomposition reaction, an excess of radioactivity corresponding to the release of $1.6\alpha X$ mg of sulfur

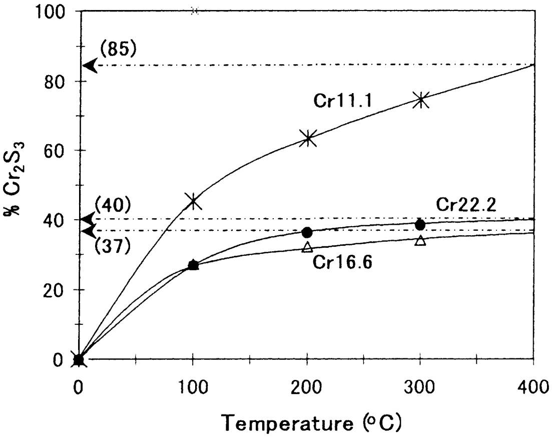

Fig. 3. Percentage of formed Cr_2S_3 at 100, 200 and 300 °C as a function of sulfidation temperature.

accumulated at lower temperatures is detected at 400 °C.

Finally, the total amount of sulfur accumulated on the catalyst after the total reaction (Eq. (3)) is $(M_S)_{Sul} - (M_S)_{Dec} = 3.2\alpha X$ (mg of sulfur).

We can obtain the value of α at 400 °C by two methods. First, we can extrapolate α at 400 °C from the results obtained for lower sulfidation temperatures. At 100, 200 and 300 °C, Cr_2S_3 species are progressively formed through CrS_x intermediate compound formation. We plotted the percentage of Cr_2S_3 formation calculated from the results of Table 1. Then, using the obtained figure (Fig. 3), we can extrapolate the percentage of Cr_2S_3 that would be formed at 400 °C if CrS decomposition would not occur, i.e. we can determine the theoretical 'α' at 400 °C. Results are reported in Table 3. This first determination method does not require any mechanistic consideration. Proposed chemical equations are used for the second method. We will base the calculation on the experimental results obtained at 400 °C. These results (Table 1), represent the mass of S contained in CrS formed from Cr_2S_3 decomposition. Therefore, it is easy to calculate the mass of sulfur that was contained in Cr_2S_3 before decomposition. By extension, we can deduce the theoretical Cr_2S_3 formation percentage at 400 °C. Calculation results are reported in Table 3 and are consistent with the results obtained by extrapolation (on Fig. 3). That means that the supported oxidic Cr phase acts somewhat like the unsupported Cr oxidic species upon sulfidation.

We can also calculate the sulfur loss observed at 400 °C. Indeed, at 400 °C, on one hand some sulfur is accumulated on the catalyst in order to complete the sulfidation of Cr_2S_3 near 400 °C (complete sulfidation of CrS_x species formed at 300 °C). This amount of sulfur accumulated between 300 and 400 °C is easily calculable from the data of Table 3 (extrapolated Cr_2S_3 formation percentages). On the other hand, it is also possible to calculate the amount of sulfur released from the catalyst by decomposition of Cr_2S_3 formed at 400 °C ($1.6X$ mg). As this latter amount is superior to the amount of sulfur necessary to complete the formation of CrS_x into Cr_2S_3 between 300 and 400 °C, a liberation of S is globally detected at 400 °C (the collected radioactivity was found to be superior to the introduced one) by the RPTM. Results of calculations are reported in Table 3 and are close to the ones observed during the experiments, confirming that the above suppositions fit rather well with the observations. The differences can be explained by the arbitrary plot of the curve used for extrapolation and also by the difficulty sometimes to collect and therefore to measure all the formed S_8 quantity with accuracy.

In brief, sulfidation process can be described as a progressive sulfidation of CrS_x species up to a Cr_2S_3

Table 3
Comparison between theoretical calculations and experimental results: percentage of Cr_2S_3 formed at 400 °C and quantity of S released at 400 °C

Catalyst	Cr_2S_3 (%) at 400 °C		Loss of S (mg g^{-1} catalyst)	
	Extrapolated from Fig. 3	Calculated from Table 1	Experimental	Calculated
Cr11.1	85	83.6	10	9.5
Cr16.6	37	40	6	7.5
Cr22.2	40	43.1	10.3	12.5
Cr22.2(S400)	–	57.7	–	–

formulation at 300–400 °C, this latter compound being further decomposed into CrS.

5. Influence of the Cr loading on the nature of the active phase

Examining Table 3, we clearly see that the percentage of sulfidation, calculated as the percentage of formed Cr_2S_3, is higher for the catalyst containing 11.1 wt.% of CrO_3 ($\sim$85%) than the ones observed for the catalyst containing 22.2 wt.% CrO_3 (between $\sim$40 and 60% according to the experimental method). A possible explanation is the difference of repartition of CrO_3 within the alumina matrix depending on the amount of deposited species. The lower dispersion in the case of 22.2 wt.% CrO_3 (as well as in the case of 16.6 wt.% CrO_3) might be due to the formation of big CrO_3 bulk particles. Formation of a surface Cr–Al mixed oxidic phase is also likely to occur, because Cr is a small atom that can therefore easily occupy the alumina surface octahedral sites to form a ruby-like structure.

If we examine the sulfur uptake of the 11.1 wt.% CrO_3 and 22.2 wt.% CrO_3 catalysts, we can see that they are almost the same (respectively, 29.7 and 30.6 mg $g_{cat}{}^{-1}$). Nevertheless, we reported in a previous paper [9] that DBT HDS conversion of the latter at 360 °C (59.1%) was superior to the one of the former (39.6%). Therefore, although the sulfur uptake is the same, activity is higher when the Cr loading is higher. Moreover, the amount of labile sulfur species on the 22.2 wt.% CrO_3 catalyst was $\sim$6.29 mg $g_{cat}{}^{-1}$, whilst it was only 3.41 mg $g_{cat}{}^{-1}$ for the 11.1 wt.% loaded one. It can be deduced that the activity variation is related to a variation in the active phase nature which permits a conversion of a greater part of the accumulated sulfur species into labile sulfur species. For low Cr loadings, it is likely that Cr is rather well dispersed on the alumina, occupying possibly a part of the alumina surface octahedral sites. The fact that $\sim$85% of the Cr is sulfided on the 11 wt.% CrO_3 catalyst reflects this rather good dispersion state. For the 22.2 wt.% CrO_3 catalysts, it is very likely that bulk Cr_2O_3 particles are created from Cr nucleation points (Cr inserted in the octahedral sites of the alumina), giving CrO_3 aggregates, of which only surfaces can be sulfided. Stack growing of supported Cr oxides seems to be a reasonable hypothesis, because Cr oxides exhibit the tendency to form lamellar stack-like structures due to the sp^3d^2 hybridization of Cr III atoms. In other words, for the low Cr loadings, the system can be represented as a CrS phase supported on alumina, whilst for the higher loadings the system can be represented as a CrS phase supported on Cr_2O_3. Cr electronegativity being higher (Allred–Rochow electronegativity = 1.56) than that of aluminum (1.47), Cr–S bonds are likely to be weakened, leading into a higher number of S labile species, even if the active phase quantity is the same. Catalyst re-oxidation experiment results are also in good agreement with this hypothesis. Indeed, whilst it was observed that re-oxidation percentage in the case of catalyst containing 11.1 wt.% CrO_3 was very low ($\sim$13% at 450 °C), it was higher for the 16.6 wt.% CrO_3 catalyst ($\sim$46% at 450 °C) and for the 22.2 wt.% CrO_3 catalyst ($\sim$65% at 450 °C and 100% at 500 °C). This can also be explained by the fact that for high Cr loadings, Cr–S bond is weakened, and CrS is therefore easily attacked by O_2 molecules, whilst in the case of low Cr loadings, CrS structure is likely to be stabilized in the alumina structure.

As another piece of evidence, the DBT HDS activity of a catalyst containing 33.3 wt.% CrO_3 was found to be even higher than the 22.2 wt.% one [9] (77.5 and 59.1%, respectively). We calculated the CrO_3 wt.% loading required for a ‘monolayer’ of Cr_2O_3 as being 20–25% for the studied alumina. It would be therefore difficult to explain the increase in activity obtained for the 33 wt.% CrO_3 catalyst by an increase in the active phase quantity, but a modification of its nature could be a satisfactory explanation that is in good agreement with the earlier discussion.

Concerning the 22.2 wt.% CrO_3-containing catalysts, the sulfidation percentage is different according to the experimental procedure. Indeed, if we compare the results for the catalyst sulfided at 100, 200, 300 and 400 °C (Cr22.2) to the one of the catalyst sulfided directly at 400 °C (Cr22.2(S400)), it is clear that the latter procedure permits one to obtain a better final sulfidation percentage (57.7% versus 43.1%). Rather, severe sulfidation conditions might permit a redistribution of the Cr_2O_3 aggregates on the surface of the catalysts, giving a better repartition of the species, leading to a better sulfidation percentage.

6. Conclusion

(1) When examining the literature, one can remark that Cr-based hydrotreating catalysts give contradictory activity results. This can be explained, at least in part, by the results of the present study. First, according to the sulfidation temperature, species present on the surface of the catalysts can vary over a wide range of compositions. These species are CrS_x intermediate species, which give Cr_2S_3 between 300 and 400 °C, itself decomposing into CrS near 400 °C. It is reasonable to think that the catalytic properties of each species are different and therefore catalytic results might vary according to the sulfidation temperature. Moreover, using different sulfidation procedures, the catalyst sulfidation percentage can also vary. Indeed, the sulfidation percentage was found to be higher on a catalyst directly sulfided at 400 °C rather than on a catalyst sulfided by steps at 100, 200, 300 and 400 °C. Catalytic results recently obtained tend to show that the DBT HDS activity over Cr-alumina catalysts is effectively higher when the direct sulfidation procedure is used rather than the stepped one (whilst doped catalysts seems to have the tendency to exhibit the reverse phenomenon). Another important point that can explain the differences observed in the literature is the formation of S_8 particles. According to the experimental conditions, they can be more or less well eliminated from the system. For example, for liquid phase reactions (such as DBT HDS) S_8 can be dissolved in the solvent (if the solvent is effective for S_8 dissolution) and removed from the reactor easily, whilst for gas phase reactions (typically thiophene HDS) they might be more difficult to eliminate. Flow rate can also play a role in the removal speed of S_8 particles formed in situ on the catalysts. In this sense, Cr-based HDS catalysts are quite difficult to handle, as formed S_8 particles can have an influence on the activity results.

(2) Increase in the DBT HDS activity observed previously when Cr loading increased could be explained by a modification of the nature of the active phase rather than an increase in its quantity. Indeed, it was observed that, using the same sulfidation conditions, for a catalyst containing 11.1 wt.% CrO_3, the amount of incorporated sulfur was the same as the one observed on a 22.2 wt.% CrO_3 catalyst. Moreover, in the second case, whilst the incorporated sulfur amount is the same, the number of formed labile sulfur atoms was found to be almost double. It was deduced that Cr_2O_3 aggregates grow (staking) on the alumina when Cr loading is increased, and only the external surface of the catalysts can be sulfided. Therefore, whilst for low Cr loadings, the active phase can be represented as a CrS phase supported on alumina, for higher Cr loadings the system is more likely to be a CrS phase supported on Cr_2O_3. In this second case, whilst accumulated sulfur quantity is low due to an increase in the unsulfided bulk Cr_2O_3 aggregates percentage, the number of labile sulfur atoms created on the aggregates surface is higher and activity increases.

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